

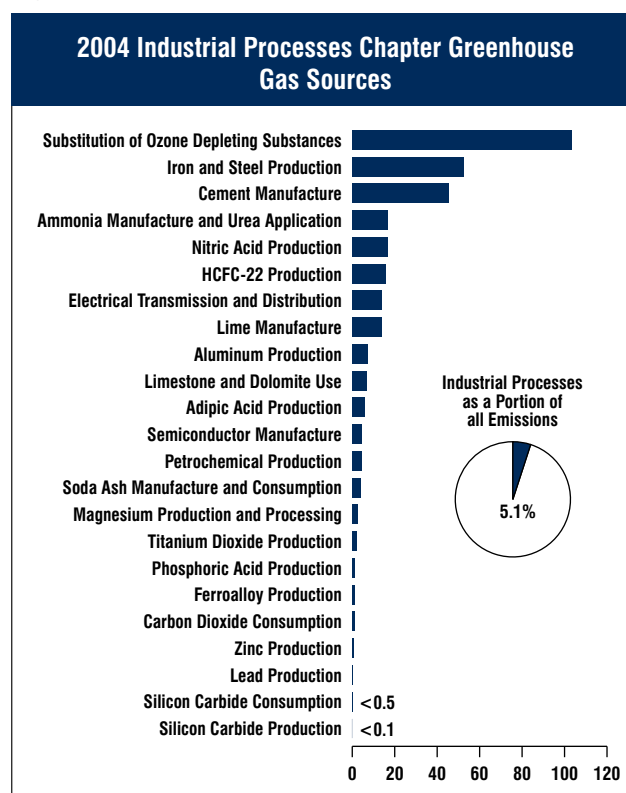
## 4. Industrial Processes

**G**reenhouse gas emissions are produced as a by-product of various non-energy-related industrial activities. That is, these emissions are produced from an industrial process itself and are not directly a result of energy consumed during the process. For example, raw materials can be chemically transformed from one state to another. This transformation can result in the release of greenhouse gases such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), or nitrous oxide (N<sub>2</sub>O). The processes addressed in this chapter include iron and steel production, cement manufacture, ammonia manufacture and urea application, lime manufacture, limestone and dolomite use (e.g., flux stone, flue gas desulfurization, and glass manufacturing), soda ash manufacture and consumption, titanium dioxide production, phosphoric acid production, ferroalloy production, CO<sub>2</sub> consumption, aluminum production, petrochemical production, silicon carbide production and consumption, lead production, zinc production, nitric acid production, and adipic acid production (see Figure 4-1).

In addition to the three greenhouse gases listed above, there are also industrial sources of man-made fluorinated compounds called hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>). The present contribution of these gases to the radiative forcing effect of all anthropogenic greenhouse gases is small; however, because of their extremely long lifetimes, many of them will continue to accumulate in the atmosphere as long as emissions continue. In addition, many of these gases have high global warming potentials; SF<sub>6</sub> is the most potent greenhouse gas the Intergovernmental Panel on Climate Change (IPCC) has evaluated. Usage of HFCs for the substitution of ozone depleting substances is growing rapidly, as they are the primary substitutes for ozone depleting substances (ODSs), which are being phased-out under the *Montreal Protocol on Substances that Deplete the Ozone Layer*. In addition to their use as ODS substitutes, HFCs, PFCs, SF<sub>6</sub>, and other fluorinated compounds are employed and emitted by a number of other industrial sources in the United States. These industries include aluminum production, HCFC-22 production, semiconductor manufacture, electric power transmission and distribution, and magnesium metal production and processing.

In 2004, industrial processes generated emissions of 320.7 teragrams of CO<sub>2</sub> equivalent (Tg CO<sub>2</sub> Eq.), or 5 percent of total U.S. greenhouse gas emissions. CO<sub>2</sub> emissions from all industrial processes were 152.6 Tg CO<sub>2</sub> Eq. (152,650 Gg) in 2004. This amount accounted for only 3 percent of

**Figure 4-1**



national CO<sub>2</sub> emissions. CH<sub>4</sub> emissions from petrochemical, silicon carbide, and iron and steel production resulted in emissions of approximately 2.7 Tg CO<sub>2</sub> Eq. (127 Gg) in 2004, which was less than 1 percent of U.S. CH<sub>4</sub> emissions. N<sub>2</sub>O emissions from adipic acid and nitric acid production were 22.4 Tg CO<sub>2</sub> Eq. (72 Gg) in 2004, or 6 percent of total U.S. N<sub>2</sub>O emissions. In 2004, combined emissions of HFCs, PFCs and SF<sub>6</sub> totaled 143.0 Tg CO<sub>2</sub> Eq. Overall, emissions from industrial processes increased by 6.5 percent from 1990 to 2004 despite decreases in emissions from several industrial processes, such as iron and steel, aluminum production, ammonia manufacture and urea application, and electrical transmission and distribution. The increase in overall emissions was driven by a rise in the emissions originating from cement manufacture and, primarily, the emissions from the use of substitutes for ODSs.

Table 4-1 summarizes emissions for the Industrial Processes chapter in units of Tg CO<sub>2</sub> Eq., while unweighted native gas emissions in gigagrams (Gg) are provided in Table 4-2.

In order to ensure the quality of the emission estimates from industrial processes, Tier 1 quality assurance and quality control (QA/QC) procedures and checks have been performed on all industrial process sources. Where performed, Tier 2 procedures focused on the emission factor and activity data sources and methodology used for estimating emissions, and will be described within the QA/QC and Verification Discussion of that source description. In addition to the national QA/QC plan, a more detailed plan was developed specifically for the CO<sub>2</sub> and CH<sub>4</sub> industrial processes sources. This plan was based on the U.S. strategy,

**Table 4-1: Emissions from Industrial Processes (Tg CO<sub>2</sub> Eq.)**

Gas/Source	1990	1998	1999	2000	2001	2002	2003	2004
<b>CO<sub>2</sub></b>	<b>174.8</b>	<b>171.9</b>	<b>167.5</b>	<b>166.4</b>	<b>152.5</b>	<b>152.6</b>	<b>147.6</b>	<b>152.6</b>
Iron and Steel Production	85.0	67.7	63.8	65.3	57.8	54.6	53.3	51.3
Cement Manufacture	33.3	39.2	40.0	41.2	41.4	42.9	43.1	45.6
Ammonia Manufacture & Urea Application	19.3	21.9	20.6	19.6	16.7	18.5	15.3	16.9
Lime Manufacture	11.2	13.9	13.5	13.3	12.8	12.3	13.0	13.7
Limestone and Dolomite Use	5.5	7.4	8.1	6.0	5.7	5.9	4.7	6.7
Aluminum Production	7.0	6.4	6.5	6.2	4.5	4.6	4.6	4.3
Soda Ash Manufacture and Consumption	4.1	4.3	4.2	4.2	4.1	4.1	4.1	4.2
Petrochemical Production	2.2	3.0	3.1	3.0	2.8	2.9	2.8	2.9
Titanium Dioxide Production	1.3	1.8	1.9	1.9	1.9	2.0	2.0	2.3
Phosphoric Acid Production	1.5	1.6	1.5	1.4	1.3	1.3	1.4	1.4
Ferroalloy Production	2.0	2.0	2.0	1.7	1.3	1.2	1.2	1.3
CO <sub>2</sub> Consumption	0.9	0.9	0.8	1.0	0.8	1.0	1.3	1.2
Zinc Production	0.9	1.1	1.1	1.1	1.0	0.9	0.5	0.5
Lead Production	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Silicon Carbide Consumption	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
<b>CH<sub>4</sub></b>	<b>2.5</b>	<b>2.9</b>	<b>2.9</b>	<b>2.9</b>	<b>2.5</b>	<b>2.5</b>	<b>2.5</b>	<b>2.7</b>
Petrochemical Production	1.2	1.7	1.7	1.7	1.4	1.5	1.5	1.6
Iron and Steel Production	1.3	1.2	1.2	1.2	1.1	1.0	1.0	1.0
Silicon Carbide Production	+	+	+	+	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>33.0</b>	<b>26.9</b>	<b>25.6</b>	<b>25.6</b>	<b>20.8</b>	<b>23.1</b>	<b>22.9</b>	<b>22.4</b>
Nitric Acid Production	17.8	20.9	20.1	19.6	15.9	17.2	16.7	16.6
Adipic Acid Production	15.2	6.0	5.5	6.0	4.9	5.9	6.2	5.7
<b>HFCs, PFCs, and SF<sub>6</sub></b>	<b>90.8</b>	<b>133.4</b>	<b>131.5</b>	<b>134.7</b>	<b>124.9</b>	<b>132.7</b>	<b>131.0</b>	<b>143.0</b>
Substitution of Ozone Depleting Substances	0.4	54.5	62.8	71.2	78.6	86.2	93.5	103.3
HCFC-22 Production	35.0	40.1	30.4	29.8	19.8	19.8	12.3	15.6
Electrical Transmission and Distribution	28.6	16.7	16.1	15.3	15.3	14.5	14.0	13.8
Semiconductor Manufacture	2.9	7.1	7.2	6.3	4.5	4.4	4.3	4.7
Aluminum Production	18.4	9.1	9.0	9.0	4.0	5.3	3.8	2.8
Magnesium Production and Processing	5.4	5.8	6.0	3.2	2.6	2.6	3.0	2.7
<b>Total</b>	<b>301.1</b>	<b>335.1</b>	<b>327.5</b>	<b>329.6</b>	<b>300.7</b>	<b>310.9</b>	<b>304.1</b>	<b>320.7</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

Note: Totals may not sum due to independent rounding.

**Table 4-2: Emissions from Industrial Processes (Gg)**

Gas/Source	1990	1998	1999	2000	2001	2002	2003	2004
<b>CO<sub>2</sub></b>	<b>174,791</b>	<b>171,897</b>	<b>167,450</b>	<b>166,379</b>	<b>152,529</b>	<b>152,605</b>	<b>147,649</b>	<b>152,650</b>
Iron and Steel Production	85,023	67,689	63,821	65,316	57,822	54,550	53,335	51,334
Cement Manufacture	33,278	39,218	39,991	41,190	41,357	42,898	43,082	45,559
Ammonia Manufacture & Urea Application	19,306	21,934	20,615	19,616	16,719	18,510	15,278	16,894
Lime Manufacture	11,242	13,919	13,473	13,322	12,828	12,309	12,987	13,698
Limestone and Dolomite Use	5,533	7,449	8,057	5,960	5,733	5,885	4,720	6,702
Aluminum Production	7,045	6,359	6,458	6,244	4,505	4,596	4,608	4,346
Soda Ash Manufacture and Consumption	4,141	4,325	4,217	4,181	4,147	4,139	4,111	4,205
Petrochemical Production	2,221	3,015	3,054	3,004	2,787	2,857	2,777	2,895
Titanium Dioxide Production	1,308	1,819	1,853	1,918	1,857	1,997	2,013	2,259
Phosphoric Acid Production	1,529	1,593	1,539	1,382	1,264	1,338	1,382	1,395
Ferroalloy Production	1,980	2,027	1,996	1,719	1,329	1,237	1,159	1,287
CO <sub>2</sub> Consumption	860	912	849	957	818	968	1,293	1,183
Zinc Production	939	1,140	1,080	1,129	976	927	502	502
Lead Production	285	308	310	311	293	290	289	259
Silicon Carbide Consumption	100	190	137	130	94	105	111	133
<b>CH<sub>4</sub></b>	<b>120</b>	<b>138</b>	<b>138</b>	<b>138</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>127</b>
Petrochemical Production	56	80	81	80	68	72	72	77
Iron and Steel Production	63	57	56	57	51	48	49	50
Silicon Carbide Production	1	1	1	1	+	+	+	+
<b>N<sub>2</sub>O</b>	<b>107</b>	<b>87</b>	<b>83</b>	<b>83</b>	<b>67</b>	<b>75</b>	<b>74</b>	<b>72</b>
Nitric Acid Production	58	67	65	63	51	56	54	54
Adipic Acid Production	49	19	18	19	16	19	20	19
<b>HFCs, PFCs, and SF<sub>6</sub></b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>	<b>M</b>
Substitution of Ozone Depleting Substances	M	M	M	M	M	M	M	M
HCFC-22 Production <sup>a</sup>	3	3	3	3	2	2	1	1
Electrical Transmission and Distribution <sup>b</sup>	1	1	1	1	1	1	1	1
Semiconductor Manufacture	M	M	M	M	M	M	M	M
Aluminum Production	M	M	M	M	M	M	M	M
Magnesium Production and Processing <sup>b</sup>	+	+	+	+	+	+	+	+
<b>NO<sub>x</sub></b>	<b>591</b>	<b>637</b>	<b>595</b>	<b>626</b>	<b>656</b>	<b>630</b>	<b>631</b>	<b>632</b>
<b>CO</b>	<b>4,124</b>	<b>3,163</b>	<b>2,156</b>	<b>2,217</b>	<b>2,339</b>	<b>2,286</b>	<b>2,286</b>	<b>2,286</b>
<b>NMVOCs</b>	<b>2,426</b>	<b>2,047</b>	<b>1,183</b>	<b>1,773</b>	<b>1,769</b>	<b>1,723</b>	<b>1,725</b>	<b>1,727</b>

+ Does not exceed 0.5 Gg  
M (Mixture of gases)  
<sup>a</sup> HFC-23 emitted  
<sup>b</sup> SF<sub>6</sub> emitted  
Note: Totals may not sum due to independent rounding.

but was tailored to include specific procedures recommended for these sources.

The general method employed to estimate emissions for industrial processes, as recommended by the IPCC, involves multiplying production data (or activity data) for each process by an emission factor per unit of production. The uncertainty of the emission estimates is therefore generally a function of a combination of the uncertainties surrounding the production and emission factor variables. Uncertainty of activity data and the associated probability density functions for industrial process CO<sub>2</sub> sources were estimated based on expert assessment of available qualitative

and quantitative information. Uncertainty estimates and probability density functions for the emission factors used to calculate emissions from this source were devised based on IPCC recommendations.

Activity data is obtained through a survey of manufacturers conducted by various organizations (specified within each source); the uncertainty of the activity data is a function of the reliability of plant-level production data and is influenced by the completeness of the survey response. The emission factors used were either derived using calculations that assume precise and efficient chemical reactions, or were based upon empirical data in published references. As a result, uncertainties in

the emission coefficients can be attributed to, among other things, inefficiencies in the chemical reactions associated with each production process or to the use of empirically-derived emission factors that are biased; therefore, they may not represent U.S. national averages. Additional assumptions are described within each source.

The uncertainty analysis performed to quantify uncertainties associated with the 2004 inventory estimates from industrial processes continues a multi-year process for developing credible quantitative uncertainty estimates for these source categories using the IPCC Tier 2 approach. As the process continues, the type and the characteristics of the actual probability density functions underlying the input variables are identified and better characterized (resulting in development of more reliable inputs for the model, including accurate characterization of correlation between variables), based primarily on expert judgment. Accordingly, the quantitative uncertainty estimates reported in this section should be considered illustrative and as iterations of ongoing efforts to produce accurate uncertainty estimates. The correlation among data used for estimating emissions for different sources can influence the uncertainty analysis of each individual source. While the uncertainty analysis recognizes very significant connections among sources, a more comprehensive approach that accounts for all linkages will be identified as the uncertainty analysis moves forward.

## 4.1. Iron and Steel Production (IPCC Source Category 2C1)

In addition to being an energy intensive process, the production of iron and steel also generates process-related emissions of CO<sub>2</sub> and CH<sub>4</sub>. Iron is produced by first reducing iron oxide (iron ore) with metallurgical coke in a blast furnace to produce pig iron (impure iron containing about 3 to 5 percent carbon by weight). Metallurgical coke is manufactured in a coke plant using coking coal as a raw material. Iron may be introduced into the blast furnace in the form of raw iron ore, pellets, briquettes, or sinter. Pig iron is used as a raw material in the production of steel (containing about 0.4 percent carbon by weight). Pig iron is also used as a raw material in the production of iron products in foundries. The pig iron production process produces CO<sub>2</sub> emissions and fugitive CH<sub>4</sub> emissions.

The production of metallurgical coke from coking coal and the consumption of the metallurgical coke used as a reducing agent in the blast furnace are considered in the inventory to be non-energy (industrial) processes, not energy (combustion) processes. Coal coke is produced by heating coking coal in a coke oven in a low-oxygen environment. The process drives off the volatile components of the coking coal and produces coal (metallurgical) coke. Coke oven gas and coal tar are carbon containing by-products of the coke manufacturing process. Coke oven gas is generally burned as a fuel within the steel mill. Coal tar is used as a raw material to produce anodes used for primary aluminum production and other electrolytic processes, and also used in the production of other coal tar products. The coke production process produces CO<sub>2</sub> emissions and fugitive CH<sub>4</sub> emissions.

Sintering is a thermal process by which fine iron-bearing particles, such as air emission control system dust, are baked, which causes the material to agglomerate into roughly one-inch pellets that are then recharged into the blast furnace for pig iron production. Iron ore particles may also be formed into larger pellets or briquettes by mechanical means, and then agglomerated by heating prior to being charged into the blast furnace. The sintering process produces CO<sub>2</sub> emissions and fugitive CH<sub>4</sub> emissions.

The metallurgical coke is a reducing agent in the blast furnace. CO<sub>2</sub> is produced as the metallurgical coke used in the blast furnace process is oxidized and the iron is reduced. Steel is produced from pig iron in a variety of specialized steel-making furnaces. The majority of CO<sub>2</sub> emissions from the iron and steel process come from the use of coke in the production of pig iron, with smaller amounts evolving from the removal of carbon from pig iron used to produce steel. Some carbon is also stored in the finished iron and steel products.

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from iron and steel production in 2004 were 51.3 Tg CO<sub>2</sub> Eq. (51,334 Gg) and 1.0 Tg CO<sub>2</sub> Eq. (50 Gg), respectively (see Table 4-3 and Table 4-4). Emissions have fluctuated significantly from 1990 to 2004 due to changes in domestic economic conditions and changes in product imports and exports. In 2004, domestic production of pig iron increased by 4.5 percent and coal coke production decreased by 1.5 percent. Overall, domestic pig iron and coke production have declined since the 1990s. Pig iron production in 2004 was 11 percent lower than in

**Table 4-3: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Tg CO<sub>2</sub> Eq.)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	85.0		67.7	63.8	65.3	57.8	54.6	53.3	51.3
CH <sub>4</sub>	1.3		1.2	1.2	1.2	1.1	1.0	1.0	1.0
<b>Total</b>	<b>86.3</b>		<b>68.9</b>	<b>65.0</b>	<b>66.5</b>	<b>58.9</b>	<b>55.6</b>	<b>54.3</b>	<b>52.4</b>

**Table 4-4: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Gg)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	85,023		67,689	63,821	65,316	57,823	54,550	53,335	51,334
CH <sub>4</sub>	63		57	56	57	51	48	49	50

2000 and 14 percent below 1990 levels. Coke production in 2004 was 19 percent lower than in 2000 and 39 percent below 1990 levels.

## Methodology

Coking coal is used to manufacture metallurgical (coal) coke that is used primarily as a reducing agent in the production of iron and steel, but is also used in the production of other metals including lead and zinc (see Lead Production and Zinc Production in this chapter). The total coking coal consumed at coke plants and the total amount of coking coal produced were identified. These data were used to estimate the emissions associated with producing coke from coking coal and attributed to the production of iron and steel. Additionally, the amount of coke consumed to produce pig iron and the emissions associated with this production were estimated. The carbon content of the coking coal and coke consumed in these processes were estimated by multiplying the energy consumption by material specific carbon-content coefficients. The carbon content coefficients used are presented in Annex 2.1.

Emissions from the re-use of scrap steel were also estimated by assuming that all the associated carbon content of the scrap steel, which has an associated carbon content of approximately 0.4 percent, are released during the scrap re-use process.

Lastly, emissions from carbon anodes, used during the production of steel in electric arc furnaces (EAFs), were also estimated. Emissions of CO<sub>2</sub> were calculated by multiplying the annual production of steel in EAFs by an emission factor (4.4 kg CO<sub>2</sub>/ton steel<sub>EAF</sub>). It was assumed that the carbon

anodes used in the production of steel in EAFs are composed of 80 percent petroleum coke and 20 percent coal tar pitch (DOE 1997). Since coal tar pitch is a by-product of the coke production process and its carbon-related emissions have already been accounted for earlier in the iron and steel emissions calculation as part of the process, the emissions were reduced by the amount of carbon in the coal tar pitch used in the anodes to avoid double counting.

Emissions associated with the production of coke from coking coal, pig iron production, the re-use of scrap steel, and the consumption of carbon anodes during the production of steel were summed.

Additionally, the coal tar pitch component of carbon anodes consumed during the production of aluminum are accounted for in the aluminum production section of this chapter. The emissions were reduced by the amount of coal tar pitch used in aluminum production to avoid double counting. The amount of coal tar pitch consumed for processes other than the aluminum production and as EAF anodes and net imports of coal tar were also estimated. A storage factor was applied to estimate emissions associated with other coal tar pitch consumption and net imports.

Carbon storage was accounted for by assuming that all domestically manufactured steel had a carbon content of 0.4 percent. Furthermore, any pig iron that was not consumed during steel production, but fabricated into finished iron products, was assumed to have a carbon content of 4 percent.

The potential CO<sub>2</sub> emissions associated with carbon contained in pig iron used for purposes other than iron and steel production, stored in the steel product, stored as coal

tar, and attributed to carbon anode consumption during aluminum production were summed and subtracted from the total emissions estimated above.

The production processes for coal coke, sinter, and pig iron result in fugitive emissions of CH<sub>4</sub>, which are emitted via leaks in the production equipment rather than through the emission stacks or vents of the production plants. The fugitive emissions were calculated by applying emission factors taken from the 1995 IPCC Guidelines (IPCC/UNEP/OECD/IEA 1995) (see Table 4-5) to annual domestic production data for coal coke, sinter, and pig iron.

Data relating to the amount of coal consumed at coke plants, and for the production of coke for domestic consumption in blast furnaces, were taken from the Energy Information Administration (EIA), *Monthly Energy Review* September 2005 (EIA 2005a); Quarterly Coal Report October through December (EIA 1998, 1999, 2000, 2001, 2002, 2003, 2004a, 2005b). Data on total coke consumed for pig iron production were taken from the American Iron and Steel Institute (AISI), *Annual Statistical Report* (AISI 2001, 2002, 2003, 2004, 2005) and provided by the AISI Annual Statistical Report (Larmoyeux 2005). Scrap steel consumption data for 1990 through 2004 were obtained from *Annual Statistical Reports* (AISI 1995, 2001, 2002, 2003,

2004, 2005) (see Table 4-6). Crude steel production, as well as pig iron use for purposes other than steel production, was also obtained from *Annual Statistical Reports* (AISI 1996, 2001, 2002, 2004, 2005). Carbon content percentages for pig iron and crude steel and the CO<sub>2</sub> emission factor for carbon anode emissions from steel production were obtained from IPCC *Good Practice Guidance* (IPCC 2000). Data on the non-energy use of coking coal were obtained from EIA's *Emissions of U.S. Greenhouse Gases in the United States* (EIA 2004b). Information on coal tar net imports was determined using data from the U.S. Bureau of the Census's U.S. International Trade Commission's Trade Dataweb (U.S. Bureau of the Census 2005). Coal tar consumption for aluminum production data was estimated based on information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program and data from USAA Primary Aluminum Statistics (USAA 2004, 2005) (see Aluminum Production in this chapter). Annual consumption of iron ore used in sinter production for 1990 through 2004 was obtained from the USGS *Iron Ore Yearbook* (USGS 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005). The CO<sub>2</sub> emission factor for carbon anode emissions from aluminum production was taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Estimates for the composition of carbon anodes used during EAF steel and aluminum production were obtained from *Energy and Environmental Profile of the U.S. Aluminum Industry* (DOE 1997).

**Table 4-5: CH<sub>4</sub> Emission Factors for Coal Coke, Sinter, and Pig Iron Production (g/kg)**

Material Produced	g CH <sub>4</sub> /kg produced
Coal Coke	0.5
Pig Iron	0.9
Sinter	0.5

Source: IPCC/UNEP/OECD/IEA 1997

## Uncertainty

The time series data sources for production of coal coke, sinter, pig iron, steel, and aluminum upon which the calculations are based are assumed to be consistent for the

**Table 4-6: Production and Consumption Data for the Calculation of CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Thousand Metric Tons)**

Gas/Activity Data	1990	1998	1999	2000	2001	2002	2003	2004
<b>CO<sub>2</sub></b>								
Coal Consumption at Coke Plants	35,269	25,573	25,499	26,254	23,655	21,461	21,998	21,473
Coke Consumption for Pig Iron	25,043	19,966	18,817	19,307	17,236	15,959	15,482	15,068
Basic Oxygen Furnace Steel Production	56,216	45,147	52,365	53,965	47,359	45,463	45,874	47,714
Electric Arc Furnace Steel Production	33,510	44,514	45,064	47,860	42,774	46,125	47,804	51,969
<b>CH<sub>4</sub></b>								
Coke Production	25,054	18,181	18,240	18,877	17,191	15,221	15,579	15,540
Iron Ore Consumption for Sinter	12,239	10,791	11,072	10,784	9,234	9,018	8,984	8,984
Domestic Pig Iron Production for Steel	49,062	47,471	45,678	47,400	41,741	39,601	40,487	42,292



entire time series. The estimates of CO<sub>2</sub> emissions from the production and utilization of coke are based on consumption data, average carbon contents, and the fraction of carbon oxidized. Uncertainty is associated with the total U.S. coke consumption and coke consumed for pig iron production. These data are provided by different data sources (EIA and AISI) and comparisons between the two datasets for net imports, production, and consumption identified discrepancies; however, the data chosen are considered the best available. These data and factors produce a relatively accurate estimate of CO<sub>2</sub> emissions. However, there are uncertainties associated with each of these factors. For example, carbon oxidation factors may vary depending on inefficiencies in the combustion process, where varying degrees of ash or soot can remain unoxidized.

Simplifying assumptions were made concerning the composition of carbon anodes (80 percent petroleum coke and 20 percent coal tar). For example, within the aluminum industry, the coal tar pitch content of anodes can vary from 15 percent in prebaked anodes to 24 to 28 percent in Soderberg anode pastes (DOE 1997). An average value was assumed and applied to all carbon anodes utilized during aluminum and steel production. The assumption is also made that all coal tar used during anode production originates as a by-product of the domestic coking process. Similarly, it was assumed that all pig iron and crude steel have carbon contents of 4 percent and 0.4 percent, respectively. The carbon content of pig iron can vary between 3 and 5 percent, while crude steel can have a carbon content of up to 2 percent, although it is typically less than 1 percent (IPCC 2000). There is also uncertainty associated with the total amount of coal tar products produced and with the storage factor for coal tar.

Uncertainty surrounding the CO<sub>2</sub> emission factor for carbon anode consumption in aluminum production was also estimated. Emissions vary depending on the specific technology used by each plant (Prebake or Soderberg). Emissions were estimated according to process and plant specific methodology outlined in the aluminum production section of this chapter. Based on expert elicitation, carbon anodes were assumed to be 20 percent coal tar pitch for the whole time series (Kantamaneni 2005). Similarly, the carbon anode emission factor for steel production can vary between 3.7 and 5.5 kg CO<sub>2</sub>/ton steel (IPCC 2000). For this analysis, the upper bound value was used.

For the purposes of the CH<sub>4</sub> calculation it is assumed that none of the CH<sub>4</sub> is captured in stacks or vents and that all of the CH<sub>4</sub> escapes as fugitive emissions. Additionally, the CO<sub>2</sub> emissions calculation is not corrected by subtracting the carbon content of the CH<sub>4</sub>, which means there may be a slight double counting of carbon as both CO<sub>2</sub> and CH<sub>4</sub>.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-7. Iron and Steel CO<sub>2</sub> emissions were estimated to be between 45.8 and 74.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 11 percent below and 45 percent above the emission estimate of 51.3 Tg CO<sub>2</sub> Eq. Iron and Steel CH<sub>4</sub> emissions were estimated to be between 1.0 Tg CO<sub>2</sub> Eq. and 1.1 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 7 percent below and 9 percent above the emission estimate of 1.0 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

Elements of the methodology to estimate CO<sub>2</sub> emissions from iron and steel production were revised for the entire

**Table 4-7: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> and CH<sub>4</sub> Emissions from Iron and Steel Production (Tg. CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Iron and Steel Production	CO <sub>2</sub>	51.3	45.8	74.5	-11%	+45%
Iron and Steel Production	CH <sub>4</sub>	1.0	1.0	1.1	-7%	+9%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

time series to include a more accurate dataset. Previously, emissions associated with the carbon content of imported pig iron were estimated and added to the total emissions associated with iron and steel production. Imported pig iron production was estimated as the difference between U.S. pig iron production and U.S. pig iron consumption. These estimates proved unreliable for 2004 warranting pursuit of new methodology.

New methods utilize data on total coke consumed for pig iron production as well as total coking coal used for coke production. EIA reports minor inconsistencies in the early years of the total U.S. coking coal datasets (EIA 1998); however, overall the datasets, which offset the need to estimate imported pig iron and coke, are believed to provide more accurate emission estimates. These changes resulted in an average annual decrease of 1.2 Tg CO<sub>2</sub> Eq. (2 percent) in CO<sub>2</sub> emissions from iron and steel production for 1990 through 2003.

## 4.2. Cement Manufacture (IPCC Source Category 2A1)

Cement manufacture is an energy- and raw-material intensive process that results in the generation of CO<sub>2</sub> from both the energy consumed in making the cement and the chemical process itself.<sup>1</sup> Cement production, at the most recent estimation, accounted for about 2.4 percent of total global industrial and energy-related CO<sub>2</sub> emissions (IPCC 1996, USGS 2003). Cement is manufactured in nearly 40 states. CO<sub>2</sub> emitted from the chemical process of cement production represents one of the largest sources of industrial CO<sub>2</sub> emissions in the United States.

During the cement production process, calcium carbonate (CaCO<sub>3</sub>) is heated in a cement kiln at a temperature of about 1,300°C (2,400°F) to form lime (i.e., calcium oxide or CaO) and CO<sub>2</sub>. This process is known as calcination or calcining. Next, the lime is combined with silica-containing materials to produce clinker (an intermediate product), with the earlier by-product CO<sub>2</sub> being released to the atmosphere. The clinker is then allowed to cool, mixed with a small amount of gypsum, and used to make Portland cement. The production of masonry cement from Portland cement requires

additional lime and, thus, results in additional CO<sub>2</sub> emissions. However, this additional lime is already accounted for in the Lime Manufacture source category in this chapter; therefore, the additional emissions from making masonry cement from clinker are not counted in this source category's total. They are presented here for informational purposes only.

In 2004, U.S. clinker production—including Puerto Rico—totaled 88,104 thousand metric tons (Van Oss 2005). The resulting emissions of CO<sub>2</sub> from 2004 cement production were estimated to be 45.6 Tg CO<sub>2</sub> Eq. (45,559 Gg) (see Table 4-8). Emissions from masonry production from clinker raw material are accounted for under Lime Manufacture.

After falling in 1991 by two percent from 1990 levels, cement production emissions have grown every year since. Overall, from 1990 to 2004, emissions increased by 37 percent. Cement continues to be a critical component of the construction industry; therefore, the availability of public construction funding, as well as overall economic growth, have had considerable influence on cement production.

### Methodology

CO<sub>2</sub> emissions from cement manufacture are created by the chemical reaction of carbon-containing minerals (i.e., calcining limestone). While in the kiln, limestone is broken down into CO<sub>2</sub> and lime with the CO<sub>2</sub> released to the atmosphere. The quantity of CO<sub>2</sub> emitted during cement production is directly proportional to the lime content of the clinker. During calcination, each mole of CaCO<sub>3</sub> (i.e.,

**Table 4-8: CO<sub>2</sub> Emissions from Cement Production (Tg CO<sub>2</sub> Eq. and Gg)\***

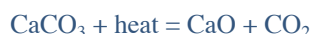
Year	Tg CO <sub>2</sub> Eq.	Gg
1990	33.3	33,278
1998	39.2	39,218
1999	40.0	39,991
2000	41.2	41,190
2001	41.4	41,357
2002	42.9	42,898
2003	43.1	43,082
2004	45.6	45,559

\* Totals exclude CO<sub>2</sub> emissions from making masonry cement from clinker, which are accounted for under Lime Manufacture.

<sup>1</sup> The CO<sub>2</sub> emissions related to the consumption of energy for cement manufacture are accounted for under CO<sub>2</sub> from Fossil Fuel Combustion in the Energy chapter.



limestone) heated in the clinker kiln forms one mole of lime (CaO) and one mole of CO<sub>2</sub>:



CO<sub>2</sub> emissions were estimated by applying an emission factor, in tons of CO<sub>2</sub> released per ton of clinker produced, to the total amount of clinker produced. The emission factor used in this analysis is the product of the average lime fraction for clinker of 64.6 percent (IPCC 2000) and a constant reflecting the mass of CO<sub>2</sub> released per unit of lime. This calculation yields an emission factor of 0.507 tons of CO<sub>2</sub> per ton of clinker produced, which was determined as follows:

$$\begin{aligned} \text{EF}_{\text{Clinker}} &= 0.646 \text{ CaO} \times \left[ \frac{44.01 \text{ g/mole CO}_2}{56.08 \text{ g/mole CaO}} \right] \\ &= 0.507 \text{ tons CO}_2/\text{ton clinker} \end{aligned}$$

During clinker production, some of the clinker precursor materials remain in the kiln as non-calcinated, partially calcinated, or fully calcinated cement kiln dust (CKD). The emissions attributable to the calcinated portion of the CKD are not accounted for by the clinker emission factor. The IPCC recommends that these additional CKD CO<sub>2</sub> emissions should be estimated as two percent of the CO<sub>2</sub> emissions calculated from clinker production. Total cement production emissions were calculated by adding the emissions from clinker production to the emissions assigned to CKD (IPCC 2000).

Masonry cement requires additional lime over and above the lime used in clinker production. In particular, non-plasticizer additives such as lime, slag, and shale are added to the cement, increasing its weight by approximately five percent. Lime accounts for approximately 60 percent of this added weight. Thus, the additional lime is equivalent to roughly 2.86 percent of the starting amount of the product, since:

$$0.6 \times 0.05 / (1 + 0.05) = 2.86\%$$

An emission factor for this added lime can then be calculated by multiplying this 2.86 percent by the molecular weight ratio of CO<sub>2</sub> to CaO (0.785) to yield 0.0224 metric tons of additional CO<sub>2</sub> emitted for every metric ton of masonry cement produced.

As previously mentioned, the CO<sub>2</sub> emissions from the additional lime added during masonry cement production are accounted for in the section on CO<sub>2</sub> emissions from Lime

Manufacture. Thus, the activity data for masonry cement production are shown in this chapter for informational purposes only, and are not included in the cement emission totals.

The 1990 through 2004 activity data for clinker and masonry cement production (see Table 4-9) were obtained through a personal communication with Hendrick Van Oss (Van Oss 2005) of the USGS and through the USGS *Mineral Yearbook: Cement* (USGS 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004). Data for 2004 clinker production were obtained from the USGS *Mineral Industry Summary: Cement* (USGS 2005). The data were compiled by USGS through questionnaires sent to domestic clinker and cement manufacturing plants.

## Uncertainty

The uncertainties contained in these estimates are primarily due to uncertainties in the lime content of clinker and in the percentage of CKD recycled inside the clinker kiln. Uncertainty is also associated with the amount of lime added to masonry cement, but it is accounted for under the Lime Manufacture source category. The lime content of clinker varies from 64 to 66 percent. CKD loss can range from 1.5 to eight percent depending upon plant specifications. Additionally, some amount of CO<sub>2</sub> is reabsorbed when the cement is used for construction. As cement reacts with water, alkaline substances such as calcium hydroxide are formed. During this curing process, these compounds may react with CO<sub>2</sub> in the atmosphere to create calcium carbonate. This reaction only occurs in roughly the outer 0.2 inches of surface

**Table 4-9: Cement Production (Gg)**

Year	Clinker	Masonry
1990	64,355	3,209
1991	62,918	2,856
1992	63,415	3,093
1993	66,957	2,975
1994	69,787	3,283
1995	71,257	3,603
1996	71,706	3,469
1997	74,112	3,634
1998	75,842	3,989
1999	77,337	4,375
2000	79,656	4,332
2001	79,979	4,450
2002	82,959	4,449
2003	83,315	4,737
2004	88,104	5,300

**Table 4-10: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Cement Manufacture (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Cement Manufacture	CO <sub>2</sub>	45.6	39.7	51.8	-13%	+14%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

area. Because the amount of CO<sub>2</sub> reabsorbed is thought to be minimal, it was not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-10. Cement Manufacture CO<sub>2</sub> emissions were estimated to be between 39.7 and 51.8 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 13 percent below and 14 percent above the emission estimate of 45.6 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

Activity data for 2003 were revised to reflect data released after the publication of the 1990 through 2003 report. The revisions resulted in a less than one percent increase in 2003 emissions.

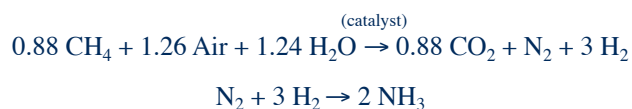
## 4.3. Ammonia Manufacture and Urea Application (IPCC Source Category 2B1)

Emissions of CO<sub>2</sub> occur during the production of synthetic ammonia, primarily through the use of natural gas as a feedstock. One nitrogen production plant located in Kansas is producing ammonia from petroleum coke feedstock. The natural gas-based, naphtha-based, and petroleum coke-based processes produce CO<sub>2</sub> and hydrogen (H<sub>2</sub>), the latter of which is used in the production of ammonia. In some plants the CO<sub>2</sub> produced is captured and used to produce urea. The brine electrolysis process for production of ammonia does not lead to process-based CO<sub>2</sub> emissions.

There are five principal process steps in synthetic ammonia production from natural gas feedstock. The primary reforming step converts CH<sub>4</sub> to CO<sub>2</sub>, carbon monoxide (CO), and H<sub>2</sub> in the presence of a catalyst. Only 30 to 40 percent of the CH<sub>4</sub> feedstock to the primary reformer is converted

to CO and CO<sub>2</sub>. The secondary reforming step converts the remaining CH<sub>4</sub> feedstock to CO and CO<sub>2</sub>. The CO in the process gas from the secondary reforming step (representing approximately 15 percent of the process gas) is converted to CO<sub>2</sub> in the presence of a catalyst, water, and air in the shift conversion step. CO<sub>2</sub> is removed from the process gas by the shift conversion process, and the hydrogen gas is combined with the nitrogen (N<sub>2</sub>) gas in the process gas during the ammonia synthesis step to produce ammonia. The CO<sub>2</sub> is included in a waste gas stream with other process impurities and is absorbed by a scrubber solution. In regenerating the scrubber solution, CO<sub>2</sub> is released.

The conversion process for conventional steam reforming of CH<sub>4</sub>, including primary and secondary reforming and the shift conversion processes, is approximately as follows:



To produce synthetic ammonia from petroleum coke, the petroleum coke is gasified and converted to CO<sub>2</sub> and H<sub>2</sub>. These gases are separated, and the H<sub>2</sub> is used as a feedstock to the ammonia production process, where it is reacted with N<sub>2</sub> to form ammonia.

Not all of the CO<sub>2</sub> produced in the production of ammonia is emitted directly to the atmosphere. Both ammonia and CO<sub>2</sub> are used as raw materials in the production of urea [CO(NH<sub>2</sub>)<sub>2</sub>], which is another type of nitrogenous fertilizer that contains carbon as well as nitrogen. The chemical reaction that produces urea is:



The carbon in the urea that is produced and assumed to be subsequently applied to agricultural land as a nitrogenous fertilizer is ultimately released into the environment as CO<sub>2</sub>; therefore, the CO<sub>2</sub> produced by ammonia production and

subsequently used in the production of urea does not change overall CO<sub>2</sub> emissions. However, the CO<sub>2</sub> emissions are allocated to the ammonia and urea production processes in accordance to the amount of ammonia and urea produced.

Net emissions of CO<sub>2</sub> from ammonia manufacture in 2004 were 9.6 Tg CO<sub>2</sub> Eq. (9,571 Gg), and are summarized in Table 4-11 and Table 4-12. Emissions of CO<sub>2</sub> from urea application in 2004 totaled 7.3 Tg CO<sub>2</sub> Eq. (7,323Gg), and are summarized in Table 4-11 and Table 4-12.

## Methodology

The calculation methodology for non-combustion CO<sub>2</sub> emissions from production of nitrogenous fertilizers from natural gas feedstock is based on a CO<sub>2</sub> emission factor published by the European Fertilizer Manufacturers Association (EFMA). The CO<sub>2</sub> emission factor (1.2 metric tons CO<sub>2</sub>/metric ton NH<sub>3</sub>) is applied to the percent of total annual domestic ammonia production from natural gas feedstock. Emissions of CO<sub>2</sub> from ammonia production are then adjusted to account for the use of some of the CO<sub>2</sub> produced from ammonia production as a raw material in the production of urea. For each ton of urea produced, 8.8 of every 12 tons of CO<sub>2</sub> are consumed and 6.8 of every 12 tons of ammonia are consumed. The CO<sub>2</sub> emissions reported for ammonia production are therefore reduced by a factor of 0.73 multiplied by total annual domestic urea production, and that amount of CO<sub>2</sub> emissions is allocated to urea fertilizer application. Total CO<sub>2</sub> emissions resulting from nitrogenous fertilizer production do not change as a result of this calculation, but some of the CO<sub>2</sub> emissions are attributed

to ammonia production and some of the CO<sub>2</sub> emissions are attributed to urea application.

The calculation of the total non-combustion CO<sub>2</sub> emissions from nitrogenous fertilizers accounts for CO<sub>2</sub> emissions from the application of imported and domestically produced urea. For each ton of imported urea applied, 0.73 tons of CO<sub>2</sub> are emitted to the atmosphere. The amount of imported urea applied is calculated based on the net of urea imports and exports.

All ammonia production and subsequent urea production are assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of ammonia production from petroleum coke feedstock at one plant located in Kansas. The CO<sub>2</sub> emission factor for production of ammonia from petroleum coke is based on plant specific data, wherein all carbon contained in the petroleum coke feedstock that is not used for urea production is assumed to be emitted to the atmosphere as CO<sub>2</sub> (Bark 2004). Ammonia and urea are assumed to be manufactured in the same manufacturing complex, as both the raw materials needed for urea production are produced by the ammonia production process. The CO<sub>2</sub> emission factor (3.57 metric tons CO<sub>2</sub>/metric ton NH<sub>3</sub>) is applied to the percent of total annual domestic ammonia production from petroleum coke feedstock.

The emission factor of 1.2 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> for production of ammonia from natural gas feedstock was taken from the EFMA Best Available Techniques publication, *Production of Ammonia* (EFMA 1995). The EFMA reported an emission factor range of 1.15 to 1.30

**Table 4-11: CO<sub>2</sub> Emissions from Ammonia Manufacture and Urea Application (Tg CO<sub>2</sub> Eq.)**

Source	1990	1998	1999	2000	2001	2002	2003	2004
Ammonia Manufacture	12.6	14.2	12.9	12.1	9.3	10.5	8.8	9.6
Urea Application	6.8	7.7	7.7	7.5	7.4	8.0	6.5	7.3
<b>Total</b>	<b>19.3</b>	<b>21.9</b>	<b>20.6</b>	<b>19.6</b>	<b>16.7</b>	<b>18.5</b>	<b>15.3</b>	<b>16.9</b>

**Table 4-12: CO<sub>2</sub> Emissions from Ammonia Manufacture and Urea Application (Gg)**

Source	1990	1998	1999	2000	2001	2002	2003	2004
Ammonia Manufacture	12,553	14,215	12,948	12,128	9,321	10,501	8,815	9,571
Urea Application	6,753	7,719	7,667	7,488	7,398	8,010	6,463	7,323
<b>Total</b>	<b>19,306</b>	<b>21,934</b>	<b>20,615</b>	<b>19,616</b>	<b>16,719</b>	<b>18,511</b>	<b>15,278</b>	<b>16,894</b>

metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub>, with 1.2 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> as a typical value. The EFMA reference also indicates that more than 99 percent of the CH<sub>4</sub> feedstock to the catalytic reforming process is ultimately converted to CO<sub>2</sub>. The emission factor of 3.57 metric ton CO<sub>2</sub>/metric ton NH<sub>3</sub> for production of ammonia from petroleum coke feedstock was developed from plant-specific ammonia production data and petroleum coke feedstock utilization data for the ammonia plant located in Kansas (Bark 2004). Ammonia and urea production data (see Table 4-13) were obtained from Coffeyville Resources (Coffeyville 2005) and the Census Bureau of the U.S. Department of Commerce (U.S. Census Bureau 1991 through 2005) as reported in *Current Industrial Reports Fertilizer Materials and Related Products* annual and quarterly reports. Import and export data for urea were obtained from the U.S. Census Bureau *Current Industrial Reports Fertilizer Materials and Related Products* annual reports (U.S. Census Bureau) for 1997 through 2004, The Fertilizer Institute (TFI 2002) for 1993 through 1996, and the United States International Trade Commission Interactive Tariff and Trade DataWeb (U.S. ITC 2002) for 1990 through 1992 (see Table 4-13).

## Uncertainty

The uncertainties presented in this section are primarily due to how accurately the emission factor used represents an average across all ammonia plants using natural gas feedstock. The EFMA reported an emission factor range of 1.15 to 1.30 ton CO<sub>2</sub>/ton NH<sub>3</sub>, with 1.2 ton CO<sub>2</sub>/ton NH<sub>3</sub> reported as a typical value. The actual emission factor depends upon the amount of air used in the ammonia production process, with 1.15 ton CO<sub>2</sub>/ton NH<sub>3</sub> being the approximate stoichiometric minimum that is achievable for the conventional reforming process. By using natural gas consumption data for each ammonia plant, more accurate estimates of CO<sub>2</sub> emissions from ammonia production could be calculated. However, these consumption data are often considered confidential. Also, natural gas is consumed at ammonia plants both as a feedstock to the reforming process and for generating process heat and steam. Natural gas consumption data, if available, would need to be divided into feedstock use (non-energy) and process heat and steam (fuel) use, as CO<sub>2</sub> emissions from fuel use and non-energy use are calculated separately.<sup>2</sup>

**Table 4-13: Ammonia Production, Urea Production, and Urea Net Imports (Gg)**

Year	Ammonia Production	Urea Production	Urea Net Imports
1990	15,425	8,124	1,086
1991	15,576	7,373	648
1992	16,261	8,142	656
1993	15,599	7,557	2,305
1994	16,211	7,584	2,249
1995	15,788	7,363	2,055
1996	16,260	7,755	1,051
1997	16,231	7,430	1,600
1998	16,761	8,042	2,483
1999	15,728	8,080	2,374
2000	14,342	6,969	3,241
2001	11,092	6,080	4,008
2002	12,577	7,038	3,884
2003	10,279	5,783	3,030
2004	10,939	5,755	4,231

<sup>2</sup> It appears that the IPCC emission factor for ammonia production of 1.5 ton CO<sub>2</sub> per ton ammonia may include both CO<sub>2</sub> emissions from the natural gas feedstock to the process and some CO<sub>2</sub> emissions from the natural gas used to generate process heat and steam for the process. Table 2-5, Ammonia Production Emission Factors, in Volume 3 of the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories Reference Manual* (IPCC 1997) includes two emission factors, one reported for Norway and one reported for Canada. The footnotes to the table indicate that the factor for Norway does not include natural gas used as fuel but that it is unclear whether the factor for Canada includes natural gas used as fuel. However, the factors for Norway and Canada are nearly identical (1.5 and 1.6 tons CO<sub>2</sub> per ton ammonia, respectively) and it is likely that if one value does not include fuel use, the other value also does not. For the conventional steam reforming process, however, the EFMA reports an emission factor range for feedstock CO<sub>2</sub> of 1.15 to 1.30 ton per ton (with a typical value of 1.2 ton per ton) and an emission factor for fuel CO<sub>2</sub> of 0.5 tons per ton. This corresponds to a total CO<sub>2</sub> emission factor for the ammonia production process, including both feedstock CO<sub>2</sub> and process heat CO<sub>2</sub>, of 1.7 ton per ton, which is closer to the emission factors reported in the *IPCC 1996 Reference Guidelines* than to the feedstock-only CO<sub>2</sub> emission factor of 1.2 ton CO<sub>2</sub> per ton ammonia reported by the EFMA. Because it appears that the emission factors cited in the *IPCC Guidelines* may actually include natural gas used as fuel, we use the 1.2 tons/ton emission factor developed by the EFMA.

Natural gas feedstock consumption data for the U.S. ammonia industry as a whole is available from the Energy Information Administration (EIA) *Manufacturers Energy Consumption Survey* (MECS) for the years 1985, 1988, 1991, 1994 and 1998 (EIA 1994, 1998). These feedstock consumption data collectively correspond to an effective average emission factor of 1.0 ton CO<sub>2</sub>/ton NH<sub>3</sub>, which appears to be below the stoichiometric minimum that is achievable for the conventional steam reforming process. The EIA data for natural gas consumption for the years 1994 and 1998 correspond more closely to the CO<sub>2</sub> emissions calculated using the EFMA emission factor than do data for previous years. The 1994 and 1998 data alone yield an effective emission factor of 1.1 ton CO<sub>2</sub>/ton NH<sub>3</sub>, corresponding to CO<sub>2</sub> emissions estimates that are approximately 1.5 Tg CO<sub>2</sub> Eq. below the estimates calculated using the EFMA emission factor of 1.2 ton CO<sub>2</sub>/ton NH<sub>3</sub>. Natural gas feedstock consumption data are not available from EIA for other years, and data for 1991 and previous years may underestimate feedstock natural gas consumption, and therefore the EFMA emission factor was used to estimate CO<sub>2</sub> emissions from ammonia production, rather than EIA data.

All ammonia production and subsequent urea production was assumed to be from the same process—conventional catalytic reforming of natural gas feedstock, with the exception of one ammonia production plant located in Kansas that is manufacturing ammonia from petroleum coke feedstock. Research indicates that there is only one U.S. plant that manufactures ammonia from petroleum coke. CO<sub>2</sub> emissions from this plant are explicitly accounted for in the Inventory estimates. No data for ammonia plants using naphtha or other feedstocks other than natural gas have been identified. Therefore, all other CO<sub>2</sub> emissions from ammonia plants are calculated using the emission factor for natural gas feedstock. However, actual emissions may differ because processes other

than catalytic steam reformation and feedstocks other than natural gas may have been used for ammonia production. Urea is also used for other purposes than as a nitrogenous fertilizer. It was assumed that 100 percent of the urea production and net imports are used as fertilizer or in otherwise emissive uses. It is also assumed that ammonia and urea are produced at collocated plants from the same natural gas raw material.

Such recovery may or may not affect the overall estimate of CO<sub>2</sub> emissions depending upon the end use to which the recovered CO<sub>2</sub> is applied. For example, research has identified one ammonia production plant that is recovering byproduct CO<sub>2</sub> for use in EOR. Such CO<sub>2</sub> is currently assumed to remain sequestered (see the section of this chapter on CO<sub>2</sub> Consumption); however, time series data for the amount of CO<sub>2</sub> recovered from this plant are not available and therefore all of the CO<sub>2</sub> produced by this plant is assumed to be emitted to the atmosphere and allocated to Ammonia Manufacture. Further research is required to determine whether byproduct CO<sub>2</sub> is being recovered from other ammonia production plants for application to end uses that are not accounted for elsewhere.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-14. Ammonia Manufacture and Urea Application CO<sub>2</sub> emissions were estimated to be between 15.5 and 18.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 16.9 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

Estimates of CO<sub>2</sub> emissions from ammonia manufacture and urea application for the years 2002 and 2003 were revised to reflect updated data from the U.S. Census Bureau and new data sources from the Coffeyville Nitrogen Plant. These changes resulted in a decrease in CO<sub>2</sub> emissions from

**Table 4-14: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Ammonia Manufacture and Urea Application (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup> (Tg CO <sub>2</sub> Eq.) (%)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ammonia Manufacture and Urea Application	CO <sub>2</sub>	16.9	15.5	18.3	-8%	+8%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



ammonia manufacture of 0.1 Tg CO<sub>2</sub> Eq. (1 percent) for 2002 and 0.3 Tg CO<sub>2</sub> Eq. (3 percent) for 2003.

## Planned Improvements

The United States recognizes that the Tier 2 methodology is preferred for estimating CO<sub>2</sub> emissions from ammonia manufacture. Historically, efforts have been made to acquire feedstock data for this source category however the relevant data were not available. In addition to some of the future work noted in the Uncertainty section, additional planned improvements for this source category include developing a plan to determine the feasibility of acquiring the relevant data for the Tier 2 assessment. If successful, the results will be included in future inventory submissions.

## 4.4. Lime Manufacture (IPCC Source Category 2A2)

Lime is an important manufactured product with many industrial, chemical, and environmental applications. Its major uses are in steel making, flue gas desulfurization (FGD) systems at coal-fired electric power plants, construction, and water purification. Lime has historically ranked fifth in total production of all chemicals in the United States. For U.S. operations, the term “lime” actually refers to a variety of chemical compounds. These include calcium oxide (CaO), or high-calcium quicklime; calcium hydroxide (Ca(OH)<sub>2</sub>), or hydrated lime; dolomitic quicklime ([CaO•MgO]); and dolomitic hydrate ([Ca(OH)<sub>2</sub>•MgO] or [Ca(OH)<sub>2</sub>•Mg(OH)<sub>2</sub>]).

Lime production involves three main processes: stone preparation, calcination, and hydration. CO<sub>2</sub> is generated during the calcination stage, when limestone—mostly calcium carbonate (CaCO<sub>3</sub>)—is roasted at high temperatures in a kiln to produce CaO and CO<sub>2</sub>. The CO<sub>2</sub> is given off as a gas and is normally emitted to the atmosphere. Some of the CO<sub>2</sub> generated during the production process, however, is recovered at some facilities for use in sugar refining and precipitated calcium carbonate (PCC)<sup>3</sup> production. It is also important to note that, for certain applications, lime reabsorbs CO<sub>2</sub> during use (see Uncertainty, below).

Lime production in the United States—including Puerto Rico—was reported to be 20,027 thousand metric

tons in 2004 (USGS 2005). This resulted in estimated CO<sub>2</sub> emissions of 13.7 Tg CO<sub>2</sub> Eq. (or 13,698 Gg) (see Table 4-15 and Table 4-16).

At the turn of the 20<sup>th</sup> century, over 80 percent of lime consumed in the United States went for construction uses. The contemporary lime market is distributed across four end-use categories as follows: metallurgical uses, 37 percent; environmental uses, 28 percent; chemical and industrial uses, 21 percent; construction uses, 13 percent; and refractory dolomite, one percent. In the construction sector, hydrated lime is still used to improve durability in plaster, stucco, and mortars. In 2004, the amount of hydrated lime used for traditional building remained unchanged from 2003 (USGS 2005).

Lime production in 2004 increased over four percent from 2003, the second annual increase in production after four

**Table 4-15: Net CO<sub>2</sub> Emissions from Lime Manufacture (Tg CO<sub>2</sub> Eq.)**

Year	Tg CO <sub>2</sub> Eq.
1990	11.2
1998	13.9
1999	13.5
2000	13.3
2001	12.8
2002	12.3
2003	13.0
2004	13.7

**Table 4-16: CO<sub>2</sub> Emissions from Lime Manufacture (Gg)**

Year	Potential	Recovered*	Net Emissions
1990	11,735	(493)	11,242
1998	14,980	(1,061)	13,919
1999	14,651	(1,188)	13,473
2000	14,554	(1,233)	13,322
2001	13,946	(1,118)	12,828
2002	13,360	(1,051)	12,309
2003	14,136	(1,149)	12,987
2004	14,823	(1,125)	13,698

\* For sugar refining and precipitated calcium carbonate production.  
Note: Totals may not sum due to independent rounding. Parentheses indicate negative values.

<sup>3</sup> Precipitated calcium carbonate is a specialty filler used in premium-quality coated and uncoated papers.



years of decline. Overall, from 1990 to 2004, lime production has increased by 26 percent. The increase in production is attributed in part to growth in demand for environmental applications, especially flue gas desulfurization technologies. In 1993, EPA completed regulations under the Clean Air Act capping sulfur dioxide (SO<sub>2</sub>) emissions from electric utilities. Lime scrubbers' high efficiencies and increasing affordability have allowed the flue gas desulfurization end-use to expand significantly over the years. Phase II of the Clean Air Act Amendments, which went into effect on January 1, 2000, remains the driving force behind the growth in the flue gas desulfurization market (USGS 2003).

## Methodology

During the calcination stage of lime manufacture, CO<sub>2</sub> is given off as a gas and normally exits the system with the stack gas. To calculate emissions, the amounts of high-calcium and dolomitic lime produced were multiplied by their respective emission factors. The emission factor is the product of a constant reflecting the mass of CO<sub>2</sub> released per unit of lime and the average calcium plus magnesium oxide (CaO • MgO) content for lime (95 percent for both types of lime). The emission factors were calculated as follows:

For high-calcium lime:

$$\frac{[(44.01 \text{ g/mole CO}_2) \div (56.08 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime})}{0.75 \text{ g CO}_2/\text{g lime}}$$

For dolomitic lime:

$$\frac{[(88.02 \text{ g/mole CO}_2) \div (96.39 \text{ g/mole CaO})] \times (0.95 \text{ CaO/lime})}{0.87 \text{ g CO}_2/\text{g lime}}$$

Production is adjusted to remove the mass of chemically combined water found in hydrated lime, using the midpoint of default ranges provided by the IPCC *Good Practice Guidance* (IPCC 2000). These factors set the chemically combined water content to 27 percent for high-calcium hydrated lime, and 24 percent for dolomitic hydrated lime.

Lime production in the United States was 20,027 thousand metric tons in 2004 (USGS 2005), resulting in potential CO<sub>2</sub> emissions of 14.8 Tg CO<sub>2</sub> Eq. Some of the CO<sub>2</sub> generated during the production process, however, was recovered for use in sugar refining and PCC production. Combined lime manufacture by these producers was 1,887 thousand metric tons in 2004. It was assumed that approximately 80 percent of the CO<sub>2</sub> involved in sugar refining and PCC was recovered, resulting in actual CO<sub>2</sub> emissions of 13.7 Tg CO<sub>2</sub> Eq.

The activity data for lime manufacture and lime consumption by sugar refining and PCC production for 1990 through 2004 (see Table 4-17) were obtained from USGS (1992 through 2004). Hydrated lime production is reported separately in Table 4-18. The CaO and CaO•MgO contents of lime were obtained from the IPCC *Good Practice Guidance* (IPCC 2000). Since data for the individual lime types (high calcium and dolomitic) was not provided prior

**Table 4-17: Lime Production and Lime Use for Sugar Refining and PCC (Gg)**

Year	High-Calcium Production <sup>a</sup>	Dolomitic Production <sup>a,b</sup>	Use for Sugar Refining and PCC
1990	12,947	2,895	826
1991	12,840	2,838	964
1992	13,307	2,925	1,023
1993	13,741	3,024	1,279
1994	14,274	3,116	1,374
1995	15,193	3,305	1,503
1996	15,856	3,434	1,429
1997	16,120	3,552	1,616
1998	16,750	3,423	1,779
1999	16,110	3,598	1,992
2000	15,850	3,621	2,067
2001	15,630	3,227	1,874
2002	14,900	3,051	1,762
2003	16,040	3,124	1,926
2004	16,500	3,527	1,887

<sup>a</sup> Includes hydrated lime.  
<sup>b</sup> Includes dead-burned dolomite.

**Table 4-18: Hydrated Lime Production (Gg)**

Year	High-Calcium Hydrate	Dolomitic Hydrate
1990	1,781	319
1991	1,841	329
1992	1,892	338
1993	1,908	342
1994	1,942	348
1995	2,027	363
1996	1,858	332
1997	1,820	352
1998	1,950	383
1999	2,010	298
2000	1,550	421
2001	2,030	447
2002	1,500	431
2003	2,140	464
2004	2,300	337

to 1997, total lime production for 1990 through 1996 was calculated according to the three year distribution from 1997 to 1999. For sugar refining and PCC, it was assumed that 100 percent of lime manufacture and consumption was high-calcium, based on communication with the National Lime Association (Males 2003).

## Uncertainty

The uncertainties contained in these estimates can be attributed to slight differences in the chemical composition of these products. Although the methodology accounts for various formulations of lime, it does not account for the trace impurities found in lime, such as iron oxide, alumina, and silica. Due to differences in the limestone used as a raw material, a rigid specification of lime material is impossible. As a result, few plants manufacture lime with exactly the same properties.

In addition, a portion of the CO<sub>2</sub> emitted during lime manufacture will actually be reabsorbed when the lime is consumed. As noted above, lime has many different chemical, industrial, environmental, and construction applications. In many processes, CO<sub>2</sub> reacts with the lime to create calcium carbonate (e.g., water softening). CO<sub>2</sub> reabsorption rates

vary, however, depending on the application. For example, 100 percent of the lime used to produce precipitated calcium carbonate reacts with CO<sub>2</sub>; whereas most of the lime used in steel making reacts with impurities such as silica, sulfur, and aluminum compounds. A detailed accounting of lime use in the United States and further research into the associated processes are required to quantify the amount of CO<sub>2</sub> that is reabsorbed.<sup>4</sup>

In some cases, lime is generated from calcium carbonate by-products at pulp mills and water treatment plants.<sup>5</sup> The lime generated by these processes is not included in the USGS data for commercial lime consumption. In the pulping industry, mostly using the Kraft (sulfate) pulping process, lime is consumed in order to causticize a process liquor (green liquor) composed of sodium carbonate and sodium sulfide. The green liquor results from the dilution of the smelt created by combustion of the black liquor where biogenic carbon is present from the wood. Kraft mills recover the calcium carbonate “mud” after the causticizing operation and calcine it back into lime—thereby generating CO<sub>2</sub>—for reuse in the pulping process. Although this re-generation of lime could be considered a lime manufacturing process, the CO<sub>2</sub> emitted during this process is mostly biogenic in origin, and therefore is not included in Inventory totals.<sup>6</sup>

In the case of water treatment plants, lime is used in the softening process. Some large water treatment plants may recover their waste calcium carbonate and calcine it into quicklime for reuse in the softening process. Further research is necessary to determine the degree to which lime recycling is practiced by water treatment plants in the United States.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-19. Lime CO<sub>2</sub> emissions were estimated to be between 12.6 and 14.8 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below and 8 percent above the emission estimate of 13.7 Tg CO<sub>2</sub> Eq.

<sup>4</sup> Representatives of the National Lime Association estimate that CO<sub>2</sub> reabsorption that occurs from the use of lime may offset as much as a quarter of the CO<sub>2</sub> emissions from calcination (Males 2003).

<sup>5</sup> Some carbide producers may also regenerate lime from their calcium hydroxide by-products, which does not result in emissions of CO<sub>2</sub>. In making calcium carbide, quicklime is mixed with coke and heated in electric furnaces. The regeneration of lime in this process is done using a waste calcium hydroxide (hydrated lime)  $[\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2]$ , not calcium carbonate  $[\text{CaCO}_3]$ . Thus, the calcium hydroxide is heated in the kiln to simply expel the water  $[\text{Ca}(\text{OH})_2 + \text{heat} \rightarrow \text{CaO} + \text{H}_2\text{O}]$  and no CO<sub>2</sub> is released.

<sup>6</sup> Based on comments submitted by and personal communication with Dr. Sergio F. Galeano, Geortia-Pacific Corporation.

**Table 4-19: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Lime Manufacture (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lime Manufacture	CO <sub>2</sub>	13.7	12.6	14.8	-8%	+8%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Recalculations Discussion

An inconsistency with the appropriate number of significant digits established by the IPCC for the water contents of hydrated lime was identified and corrected for the entire time series. The adjustment increased annual emission estimates throughout the time series by less than one percent relative to the previous Inventory report. The 2003 data used to estimate CO<sub>2</sub> recovery from PCC and sugar refining were updated to reflect revisions to USGS data, but the revision did not result in a net change in CO<sub>2</sub> recovery, thus net lime emissions were unchanged for 2003.

## 4.5. Limestone and Dolomite Use (IPCC Source Category 2A3)

Limestone (CaCO<sub>3</sub>) and dolomite (CaCO<sub>3</sub>MgCO<sub>3</sub>)<sup>7</sup> are basic raw materials used by a wide variety of industries, including construction, agriculture, chemical, metallurgy, glass manufacture, and environmental pollution control. Limestone is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Large deposits of limestone occur in nearly every state in the United

States, and significant quantities are extracted for industrial applications. For some of these applications, limestone is sufficiently heated during the process to generate CO<sub>2</sub> as a by-product. Examples of such applications include limestone used as a flux or purifier in metallurgical furnaces, as a sorbent in flue gas desulfurization systems for utility and industrial plants, or as a raw material in glass manufacturing and magnesium production.

In 2004, approximately 10,487 thousand metric tons of limestone and 4,373 thousand metric tons of dolomite were consumed for these applications. Overall, usage of limestone and dolomite resulted in aggregate CO<sub>2</sub> emissions of 6.7 Tg CO<sub>2</sub> Eq. (6,702 Gg) (see Table 4-20 and Table 4-21). Emissions in 2004 increased 42 percent from the previous year and have increased 21 percent overall from 1990 through 2004.

## Methodology

CO<sub>2</sub> emissions were calculated by multiplying the quantity of limestone or dolomite consumed by the average carbon content, approximately 12.0 percent for limestone and 13.2 percent for dolomite (based on stoichiometry).

**Table 4-20: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Tg CO<sub>2</sub> Eq.)**

Activity	1990	1998	1999	2000	2001	2002	2003	2004
Flux Stone	3.0	5.1	6.0	2.8	2.5	2.4	2.1	4.1
Glass Making	0.2	0.2	0	0.4	0.1	0.2	0.3	0.4
FGD	1.4	1.2	1.2	1.8	2.6	2.8	1.9	1.9
Magnesium Production	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0
Other Miscellaneous Uses	0.8	0.9	0.7	0.9	0.5	0.7	0.4	0.4
<b>Total</b>	<b>5.5</b>	<b>7.4</b>	<b>8.1</b>	<b>6.0</b>	<b>5.7</b>	<b>5.9</b>	<b>4.7</b>	<b>6.7</b>

Notes: Totals may not sum due to independent rounding. "Other miscellaneous uses" include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

<sup>7</sup> Limestone and dolomite are collectively referred to as limestone by the industry, and intermediate varieties are seldom distinguished.

**Table 4-21: CO<sub>2</sub> Emissions from Limestone & Dolomite Use (Gg)**

Activity	1990	1998	1999	2000	2001	2002	2003	2004
Flux Stone	2,999	5,132	6,030	2,830	2,514	2,405	2,072	4,112
Limestone	2,554	4,297	4,265	1,810	1,640	1,330	904	2,023
Dolomite	446	835	1,765	1,020	874	1,075	1,168	2,088
Glass Making	217	157	0	368	113	61	337	350
Limestone	189	65	0	368	113	61	337	350
Dolomite	28	91	0	0	0	0	0	0
FGD	1,433	1,230	1,240	1,774	2,551	2,766	1,932	1,871
Magnesium Production	64	73	73	73	53	0	0	0
Other Miscellaneous Uses	819	858	713	916	501	652	380	369
<b>Total</b>	<b>5,533</b>	<b>7,449</b>	<b>8,057</b>	<b>5,960</b>	<b>5,733</b>	<b>5,885</b>	<b>4,720</b>	<b>6,702</b>

Notes: Totals may not sum due to independent rounding. "Other miscellaneous uses" include chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining.

This assumes that all carbon is oxidized and released. This methodology was used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining and then converting to CO<sub>2</sub> using a molecular weight ratio.

Traditionally, the production of magnesium metal was the only other use of limestone and dolomite that produced CO<sub>2</sub> emissions. At the start of 2001, there were two magnesium production plants operating in the United States and they used different production methods. One plant produced magnesium metal using a dolomitic process that resulted in the release of CO<sub>2</sub> emissions, while the other plant produced magnesium from magnesium chloride using a CO<sub>2</sub>-emissions-free process called electrolytic reduction. However, the plant utilizing the dolomitic process ceased its operations prior to the end of 2001, so beginning in 2002 there were no emissions from this particular sub-use.

Consumption data for 1990 through 2004 of limestone and dolomite used for flux stone, glass manufacturing, flue gas desulfurization systems, chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining (see Table 4-22) were obtained from personal communication with Valentine Tepordei of the USGS (Tepordei 2005) and in the USGS *Minerals Yearbook: Crushed Stone Annual Report* (USGS 1993, 1995a, 1995b, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002a, 2003a, 2004a). The production capacity data for 1990 through 2003 of dolomitic magnesium metal (see Table 4-23) also came from the USGS (1995c, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002b, 2003b, 2004b, 2005). The last plant in the United States that used the dolomitic production process for magnesium metal closed in 2001. The USGS does not mention this process in the 2004 *Minerals Yearbook: Magnesium*; therefore, it is assumed that this process continues to be non-existent in the United States (USGS

**Table 4-22: Limestone and Dolomite Consumption (Thousand Metric Tons)**

Activity	1990	1998	1999	2000	2001	2002	2003	2004
Flux Stone	6,738	11,514	13,390	6,249	5,558	5,275	4,501	8,971
Limestone	5,804	9,767	9,694	4,114	3,727	3,023	2,055	4,599
Dolomite	933	1,748	3,696	2,135	1,831	2,252	2,466	4,373
Glass Making	489	340	0	836	258	139	765	796
Limestone	430	149	0	836	258	139	765	796
Dolomite	59	191	0	0	0	0	0	0
FGD	3,258	2,795	2,819	4,031	5,798	6,286	4,390	4,253
Other Miscellaneous Uses	1,835	1,933	1,620	2,081	1,138	1,483	863	840
<b>Total</b>	<b>12,319</b>	<b>16,582</b>	<b>17,830</b>	<b>13,197</b>	<b>12,751</b>	<b>13,183</b>	<b>10,520</b>	<b>14,859</b>

Notes: "Other miscellaneous uses" includes chemical stone, mine dusting or acid water treatment, acid neutralization, and sugar refining. Zero values for limestone and dolomite consumption for glass making result during years when the USGS reports that no limestone or dolomite are consumed for this use.

**Table 4-23: Dolomitic Magnesium Metal Production Capacity (Metric Tons)**

Year	Production Capacity
1990	35,000
1991	35,000
1992	14,909
1993	12,964
1994	21,111
1995	22,222
1996	40,000
1997	40,000
1998	40,000
1999	40,000
2000	40,000
2001	29,167
2002	0
2003	0
2004	0

Note: Production capacity for 2002, 2003, and 2004 amounts to zero because the last U.S. production plant employing the dolomitic process shut down mid-2001 (USGS 2002).

2005). During 1990 and 1992, the USGS did not conduct a detailed survey of limestone and dolomite consumption by end-use. Consumption for 1990 was estimated by applying the 1991 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to 1990 total use. Similarly, the 1992 consumption figures were approximated by applying an average of the 1991 and 1993 percentages of total limestone and dolomite use constituted by the individual limestone and dolomite uses to the 1992 total.

Additionally, each year the USGS withholds data on certain limestone and dolomite end-uses due to confidentiality agreements regarding company proprietary data. For the purposes of this analysis, emissive end-uses that contained withheld data were estimated using one of the following techniques: (1) the value for all the withheld data points for limestone or dolomite use was distributed evenly to all withheld end-uses; (2) the average percent of total limestone or dolomite for the withheld end-use in the preceding and succeeding years; or (3) the average fraction of total limestone or dolomite for the end-use over the entire time period.

Finally, there is a large quantity of crushed stone reported to the USGS under the category “unspecified uses.”

A portion of this consumption is believed to be limestone or dolomite used for emissive end uses. The quantity listed for “unspecified uses” was, therefore, allocated to each reported end-use according to each end uses fraction of total consumption in that year.<sup>8</sup>

## Uncertainty

The uncertainty levels presented in this section arise in part due to variations in the chemical composition of limestone. In addition to calcium carbonate, limestone may contain smaller amounts of magnesia, silica, and sulfur. The exact specifications for limestone or dolomite used as flux stone vary with the pyrometallurgical process, the kind of ore processed, and the final use of the slag. Similarly, the quality of the limestone used for glass manufacturing will depend on the type of glass being manufactured.

The estimates below also account for uncertainty associated with activity data. Much of the limestone consumed in the United States is reported as “other unspecified uses;” therefore, it is difficult to accurately allocate this unspecified quantity to the correct end-uses. Also, some of the limestone reported as “limestone” is believed to actually be dolomite, which has a higher carbon content. Additionally, there is significant inherent uncertainty associated with estimating withheld data points for specific end uses of limestone and dolomite. Lastly, the uncertainty of the estimates for limestone used in glass making is especially high. Large fluctuations in reported consumption exist, reflecting year-to-year changes in the number of survey responders. The uncertainty resulting from a shifting survey population is exacerbated by the gaps in the time series of reports. However, since glass making accounts for a small percent of consumption, its contribution to the overall emissions estimate is low.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-24. Limestone and Dolomite Use CO<sub>2</sub> emissions were estimated to be between 6.2 and 7.2 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 7 percent below and 8 percent above the emission estimate of 6.7 Tg CO<sub>2</sub> Eq.

<sup>8</sup> This approach was recommended by USGS.

**Table 4-24: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Limestone and Dolomite Use (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Limestone and Dolomite Use	CO <sub>2</sub>	6.7	6.2	7.2	-7%	+8%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 4.6. Soda Ash Manufacture and Consumption (IPCC Source Category 2A4)

Soda ash (sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>) is a white crystalline solid that is readily soluble in water and strongly alkaline. Commercial soda ash is used as a raw material in a variety of industrial processes and in many familiar consumer products such as glass, soap and detergents, paper, textiles, and food. It is used primarily as an alkali, either in glass manufacturing or simply as a material that reacts with and neutralizes acids or acidic substances. Internationally, two types of soda ash are produced—natural and synthetic. The United States produces only natural soda ash and is second only to China in total soda ash-production. Trona is the principal ore from which natural soda ash is made.

Only three states produce natural soda ash: Wyoming, California, and Colorado. Of these three states, only net emissions of CO<sub>2</sub> from Wyoming were calculated. This difference is a result of the production processes employed in each state.<sup>9</sup> During the production process used in Wyoming, trona ore is treated to produce soda ash. CO<sub>2</sub> is generated as a by-product of this reaction, and is eventually emitted into the atmosphere. In addition, CO<sub>2</sub> may also be released when soda ash is consumed.

In 2004, CO<sub>2</sub> emissions from the manufacture of soda ash from trona were approximately 1.6 Tg CO<sub>2</sub> Eq. (1,607 Gg). Soda ash consumption in the United States generated 2.6 Tg CO<sub>2</sub> Eq. (2,598 Gg) in 2004. Total emissions from soda ash manufacture in 2004 were 4.2 Tg CO<sub>2</sub> Eq. (4,205 Gg) (see Table 4-25 and Table 4-26). Emissions have

fluctuated since 1990. These fluctuations were strongly related to the behavior of the export market and the U.S. economy. Emissions in 2004 increased by approximately 2 percent from the previous year, and have increased overall by approximately 2 percent since 1990.

**Table 4-25: CO<sub>2</sub> Emissions from Soda Ash Manufacture and Consumption (Tg CO<sub>2</sub> Eq.)**

Year	Manufacture	Consumption	Total
1990	1.4	2.7	4.1
1998	1.6	2.7	4.3
1999	1.5	2.7	4.2
2000	1.5	2.7	4.2
2001	1.5	2.6	4.1
2002	1.5	2.7	4.1
2003	1.5	2.6	4.1
2004	1.6	2.6	4.2

Note: Totals may not sum due to independent rounding.

**Table 4-26: CO<sub>2</sub> Emissions from Soda Ash Manufacture and Consumption (Gg)**

Year	Manufacture	Consumption	Total
1990	1,431	2,710	4,141
1998	1,607	2,718	4,324
1999	1,548	2,668	4,217
2000	1,529	2,652	4,181
2001	1,500	2,648	4,147
2002	1,470	2,668	4,139
2003	1,509	2,602	4,111
2004	1,607	2,598	4,205

Note: Totals may not sum due to independent rounding.

<sup>9</sup> In California, soda ash is manufactured using sodium carbonate-bearing brines instead of trona ore. To extract the sodium carbonate, the complex brines are first treated with CO<sub>2</sub> in carbonation towers to convert the sodium carbonate into sodium bicarbonate, which then precipitates from the brine solution. The precipitated sodium bicarbonate is then calcined back into sodium carbonate. Although CO<sub>2</sub> is generated as a by-product, the CO<sub>2</sub> is recovered and recycled for use in the carbonation stage and is not emitted.

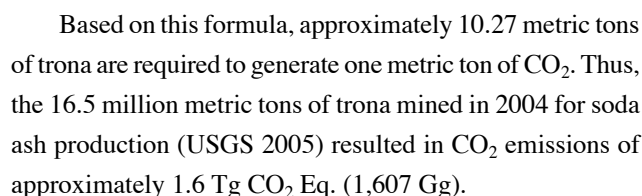


Although the United States continues to be a major supplier of world soda ash, China's soda ash production surpassed the United States in 2003, and continued to be higher than the United States in 2004. The trend is expected to continue, as will the strict competition in Asian markets. The world market for soda ash is expected to grow 2.0 to 2.5 percent annually (USGS 2005).

During the production process, trona ore is calcined in a rotary kiln and chemically transformed into a crude soda ash that requires further processing. CO<sub>2</sub> and water are generated

Year	Manufacture*	Consumption
1990	14,700	6,530
1991	14,700	6,280
1992	14,900	6,320
1993	14,500	6,280
1994	14,600	6,260
1995	16,500	6,500
1996	16,300	6,390
1997	17,100	6,480
1998	16,500	6,550
1999	15,900	6,430
2000	15,700	6,390
2001	15,400	6,380
2002	15,100	6,430
2003	15,500	6,270
2004	16,500	6,260

as by-products of the calcination process. CO<sub>2</sub> emissions from the calcination of trona can be estimated based on the following chemical reaction:



Once manufactured, most soda ash is consumed in glass and chemical production, with minor amounts in soap and detergents, pulp and paper, flue gas desulfurization and water treatment. As soda ash is consumed for these purposes, additional CO<sub>2</sub> is usually emitted. In these applications, it is assumed that one mole of carbon is released for every mole of soda ash used. Thus, approximately 0.113 metric tons of carbon (or 0.415 metric tons of CO<sub>2</sub>) are released for every metric ton of soda ash consumed.

The activity data for trona production and soda ash consumption (see Table 4-27) were taken from USGS (1994 through 2004). Soda ash manufacture and consumption data were collected by the USGS from voluntary surveys of the U.S. soda ash industry.

Emission estimates from soda ash manufacture have relatively low associated uncertainty levels in that reliable and accurate data sources are available for the emission factor and activity data. The primary source of uncertainty, however, results from the fact that emissions from soda ash consumption are dependent upon the type of processing employed by each end-use. Specific information characterizing the emissions from each end-use is limited.

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Soda Ash Manufacture and Consumption	CO <sub>2</sub>	4.2	3.9	4.5	-7%	+7%

## Industrial Processes 4-21

Therefore, there is uncertainty surrounding the emission factors from the consumption of soda ash.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-28. Soda Ash Manufacture and Consumption CO<sub>2</sub> emissions were estimated to be between 3.9 and 4.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 7 percent below and 7 percent above the emission estimate of 4.2 Tg CO<sub>2</sub> Eq.

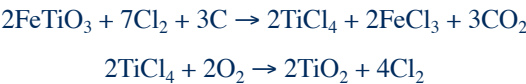
### Planned Improvements

Emissions from soda ash production in Colorado, which is produced using the nahcolite production process, will be investigated for inclusion in future inventories.

## 4.7. Titanium Dioxide Production (IPCC Source Category 2B5)

Titanium dioxide (TiO<sub>2</sub>) is a metal oxide manufactured from titanium ore, and is principally used as a pigment. Titanium dioxide is a principal ingredient in white paint, and is also used as a pigment in the manufacture of white paper, foods, and other products. There are two processes for making TiO<sub>2</sub>: the chloride process and the sulfate process. The chloride process uses petroleum coke and chlorine as raw materials and emits process-related CO<sub>2</sub>. The sulfate process does not use petroleum coke or other forms of carbon as a raw material and does not emit CO<sub>2</sub>.

The chloride process is based on the following chemical reactions:



**Table 4-29: CO<sub>2</sub> Emissions from Titanium Dioxide (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.3	1,308
1998	1.8	1,819
1999	1.9	1,853
2000	1.9	1,918
2001	1.9	1,857
2002	2.0	1,997
2003	2.0	2,013
2004	2.3	2,259

The carbon in the first chemical reaction is provided by petroleum coke, which is oxidized in the presence of the chlorine and FeTiO<sub>3</sub> (the Ti-containing ore) to form CO<sub>2</sub>. The majority of U.S. TiO<sub>2</sub> was produced in the United States through the chloride process, and a special grade of petroleum coke is manufactured specifically for this purpose. Emissions of CO<sub>2</sub> from TiO<sub>2</sub> production in 2004 were 2.3 Tg CO<sub>2</sub> Eq. (2,259 Gg), an increase of 11 percent from the previous year and 73 percent from 1990, due to increasing production within the industry (see Table 4-29).

### Methodology

Emissions of CO<sub>2</sub> from TiO<sub>2</sub> production were calculated by multiplying annual TiO<sub>2</sub> production by chloride-process-specific emission factors.

Data were obtained for the total amount of TiO<sub>2</sub> produced each year, and it was assumed that 97 percent of the total production in 2004 was produced using the chloride process. It was assumed that TiO<sub>2</sub> was produced using the chloride-process and the sulfate process in the same ratio as the ratio of the total U.S. production capacity for each process. An emission factor of 0.4 metric tons C/metric ton TiO<sub>2</sub> was applied to the estimated chloride process production. It was assumed that all TiO<sub>2</sub> produced using the chloride process was produced using petroleum coke, although some TiO<sub>2</sub> may have been produced with graphite or other carbon inputs. The amount of petroleum coke consumed annually in TiO<sub>2</sub> production was calculated based on the assumption that petroleum coke used in the process is 90 percent carbon and 10 percent inert materials.

The emission factor for the TiO<sub>2</sub> chloride process was taken from the report, *Everything You've Always Wanted to Know about Petroleum Coke* (Onder and Bagdoyan 1993). Titanium dioxide production data for 1990 through 2004 (see Table 4-30) were obtained from personal communication with Joseph Gambogi, USGS Commodity Specialist, of the USGS (Gambogi 2005) and through the *Minerals Yearbook: Titanium Annual Report* (USGS 1991 through 2003). Data for the percentage of the total TiO<sub>2</sub> production capacity that is chloride-process for 1994 through 2002 were also taken from the USGS *Minerals Yearbook* and from Joseph Gambogi for 2004. Percentage chloride-process data were not available for 1990 through 1993, and data from the 1994 USGS *Minerals Yearbook* were used for these years. Because a sulfate-process plant closed in September 2001,

**Table 4-30: Titanium Dioxide Production (Gg)**

Year	Gg
1990	979
1991	992
1992	1,140
1993	1,160
1994	1,250
1995	1,250
1996	1,230
1997	1,340
1998	1,330
1999	1,350
2000	1,400
2001	1,330
2002	1,410
2003	1,420
2004	1,540

the chloride-process percentage for 2001 was estimated based on a discussion with Joseph Gambogi (2002). By 2002, only one sulfate plant remained online in the United States. The composition data for petroleum coke were obtained from Onder and Bagdoyan (1993).

## Uncertainty

Although some TiO<sub>2</sub> may be produced using graphite or other carbon inputs, information and data regarding these practices were not available. Titanium dioxide produced using graphite inputs, for example, may generate differing amounts of CO<sub>2</sub> per unit of TiO<sub>2</sub> produced as compared to that generated through the use of petroleum coke in production. While the most accurate method to estimate emissions would be to base calculations on the amount of reducing agent used in each process rather than on the amount of TiO<sub>2</sub> produced, sufficient data were not available to do so.

Also, annual TiO<sub>2</sub> is not reported by USGS by the type of production process used (chloride or sulfate). Only

the percentage of total production capacity by process is reported. The percent of total TiO<sub>2</sub> production capacity that was attributed to the chloride process was multiplied by total TiO<sub>2</sub> production to estimate the amount of TiO<sub>2</sub> produced using the chloride process. This assumes that the chloride-process plants and sulfate-process plants operate at the same level of utilization. Finally, the emission factor was applied uniformly to all chloride-process production, and no data were available to account for differences in production efficiency among chloride process plants. In calculating the amount of petroleum coke consumed in chloride process TiO<sub>2</sub> production, literature data were used for petroleum coke composition. Certain grades of petroleum coke are manufactured specifically for use in the TiO<sub>2</sub> chloride process; however, this composition information was not available.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-31. Titanium dioxide consumption CO<sub>2</sub> emissions were estimated to be between 1.9 and 2.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 16 percent below and 16 percent above the emission estimate of 2.3 Tg CO<sub>2</sub> Eq.

## 4.8. Phosphoric Acid Production (IPCC Source Category 2A7)

Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is a basic raw material in the production of phosphate-based fertilizers. Phosphate rock is mined in Florida, North Carolina, Idaho, Utah, and other areas of the United States and is used primarily as a raw material for phosphoric acid production. The production of phosphoric acid from phosphate rock produces byproduct gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), referred to as phosphogypsum.

The composition of natural phosphate rock varies depending upon the location where it is mined. Natural phosphate rock mined in the United States generally

**Table 4-31: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Titanium Dioxide Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Titanium Dioxide Production	CO <sub>2</sub>	2.3	1.9	2.6	-16%	+16%

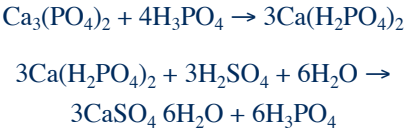
<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

contains inorganic carbon in the form of calcium carbonate (limestone) and also may contain organic carbon. The chemical composition of phosphate rock (francolite) mined in Florida is:



The calcium carbonate component of the phosphate rock is integral to the phosphate rock chemistry. Phosphate rock can also contain organic carbon that is physically incorporated into the mined rock but is not an integral component of the phosphate rock chemistry. Phosphoric acid production from natural phosphate rock is a source of CO<sub>2</sub> emissions, due to the chemical reaction of the inorganic carbon (calcium carbonate) component of the phosphate rock.

The phosphoric acid production process involves chemical reaction of the calcium phosphate (Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>) component of the phosphate rock with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and recirculated phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) (EFMA 1997). The primary chemical reactions for the production of phosphoric acid from phosphate rock are:



The limestone (CaCO<sub>3</sub>) component of the phosphate rock reacts with the sulfuric acid in the phosphoric acid production process to produce calcium sulfate (phosphogypsum) and CO<sub>2</sub>. The chemical reaction for the limestone–sulfuric acid reaction is:



Total marketable phosphate rock production in 2004 was 39.0 million metric tons. Approximately 81 percent of domestic phosphate rock production was mined in Florida and North Carolina, while approximately 13 percent of production was mined in Idaho and Utah. In addition, 2.5 million metric tons of crude phosphate rock was imported for consumption in 2004. Marketable phosphate rock production, including domestic production and imports for consumption, increased by approximately 4.2 percent between 2003 and 2004. However, over the 1990 to 2004 period, production decreased by 11 percent. The 35.3 million metric tons produced in 2001 was the lowest production level recorded since 1965 and was driven by a worldwide decrease in demand for phosphate fertilizers. Total CO<sub>2</sub> emissions from

phosphoric acid production were 1.4 Tg CO<sub>2</sub> Eq. (1,395 Gg) in 2004 (see Table 4-32).

## Methodology

CO<sub>2</sub> emissions from production of phosphoric acid from phosphate rock is calculated by multiplying the average amount of calcium carbonate contained in the natural phosphate rock by the amount of phosphate rock that is used annually to produce phosphoric acid, accounting for domestic production and net imports for consumption.

The USGS reports in the *Minerals Yearbook, Phosphate Rock*, the aggregate amount of phosphate rock mined annually in Florida and North Carolina and the aggregate amount of phosphate rock mined annually in Idaho and Utah, and reports the annual amounts of phosphate rock exported and imported for consumption (see Table 4-33). Data for domestic production of phosphate rock, exports of phosphate rock, and imports of phosphate rock for consumption for 1990 through 2004 were obtained from *USGS Minerals Yearbook, Phosphate Rock* (USGS 1994 through 2005). In 2004, the USGS reported no exports of phosphate rock from U.S. producers (USGS 2005).

The carbonate content of phosphate rock varies depending upon where the material is mined. Composition data for domestically mined and imported phosphate rock were provided by the Florida Institute of Phosphate Research (FIPR 2003). Phosphate rock mined in Florida contains approximately 3.5 percent inorganic carbon (as CO<sub>2</sub>), and phosphate rock imported from Morocco contains approximately 5 percent inorganic carbon (as CO<sub>2</sub>). Calcined phosphate rock mined in North Carolina and Idaho contains

**Table 4-32: CO<sub>2</sub> Emissions from Phosphoric Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	1.5	1,529
1998	1.6	1,593
1999	1.5	1,539
2000	1.4	1,382
2001	1.3	1,264
2002	1.3	1,338
2003	1.4	1,382
2004	1.4	1,395

**Table 4-33: Phosphate Rock Domestic Production, Exports, and Imports (Gg)**

Location/Year	1990	1998	1999	2000	2001	2002	2003	2004
U.S. Production	49,800	43,640	41,440	37,370	32,830	34,720	36,410	36,530
FL & NC	42,494	38,000	35,900	31,900	28,100	29,800	31,300	31,600
ID & UT	7,306	5,640	5,540	5,470	4,730	4,920	5,110	4,930
Exports—FL & NC	6,240	378	272	299	9	62	64	—
Imports—Morocco	451	1,760	2,170	1,930	2,500	2,700	2,400	2,500
<b>Total U.S. Consumption</b>	<b>44,011</b>	<b>45,022</b>	<b>43,338</b>	<b>39,001</b>	<b>35,321</b>	<b>37,358</b>	<b>38,746</b>	<b>39,030</b>

Source: USGS 2005, 2004, 2003, 2002, 2001, 2000, 1999, 1998, 1997, 1996, 1995.

- Assumed equal to zero.

approximately 1.5 percent and 1.0 percent inorganic carbon (as CO<sub>2</sub>), respectively (see Table 4-34).

Carbonate content data for phosphate rock mined in Florida are used to calculate the CO<sub>2</sub> emissions from consumption of phosphate rock mined in Florida and North Carolina (81 percent of domestic production) and carbonate content data for phosphate rock mined in Morocco are used to calculate CO<sub>2</sub> emissions from consumption of imported phosphate rock. The CO<sub>2</sub> emissions calculation is based on the assumption that all of the domestic production of phosphate rock is used in uncalcined form. The USGS reported that one phosphate rock producer in Idaho is producing calcined phosphate rock; however, no production data were available for this single producer (USGS 2003). Carbonate content data for uncalcined phosphate rock mined in Idaho and Utah (13 percent of domestic production) were not available, and carbonate content was therefore estimated from the carbonate content data for calcined phosphate rock mined in Idaho.

The CO<sub>2</sub> emissions calculation methodology is based on the assumption that all of the inorganic carbon (calcium carbonate) content of the phosphate rock reacts to CO<sub>2</sub> in the phosphoric acid production process and is emitted with the stack gas. The methodology also assumes that none of the

organic carbon content of the phosphate rock is converted to CO<sub>2</sub> and that all of the organic carbon content remains in the phosphoric acid product.

## Uncertainty

Phosphate rock production data used in the emission calculations are developed by the USGS through monthly and semiannual voluntary surveys of the eleven companies that owned phosphate rock mines during 2004. The phosphate rock production data are not considered to be a significant source of uncertainty because all eleven of the domestic phosphate rock producers report their annual production to the USGS. Data for imports for consumption and exports of phosphate rock used in the emission calculation are based on international trade data collected by the U.S. Census Bureau. These U.S. government economic data are not considered to be a significant source of uncertainty.

One source of potentially significant uncertainty in the calculation of CO<sub>2</sub> emissions from phosphoric acid production is the data for the carbonate composition of phosphate rock. The composition of phosphate rock varies depending upon where the material is mined, and may also vary over time. Only one set of data from the Florida

**Table 4-34: Chemical Composition of Phosphate Rock (percent by weight)**

Composition	Central Florida	North Florida	North Carolina (calcined)	Idaho (calcined)	Morocco
Total Carbon (as C)	1.60	1.76	0.76	0.60	1.56
Inorganic Carbon (as C)	1.00	0.93	0.41	0.27	1.46
Organic Carbon (as C)	0.60	0.83	0.35	—	0.10
Inorganic Carbon (as CO <sub>2</sub> )	3.67	3.43	1.50	1.00	5.00

Source: FIPR 2003

- Assumed equal to zero.



Institute of Phosphate Research (FIPR) was available for the composition of phosphate rock mined domestically and imported, and data for uncalcined phosphate rock mined in North Carolina and Idaho were unavailable. Inorganic carbon content (as CO<sub>2</sub>) of phosphate rock could vary  $\pm 1$  percent from the data included in Table 4-34, resulting in a variation in CO<sub>2</sub> emissions of  $\pm 20$  percent. Another source of uncertainty is the disposition of the organic carbon content of the phosphate rock. A representative of the FIPR indicated that in the phosphoric acid production process the organic carbon content of the mined phosphate rock generally remains in the phosphoric acid product, which is what produces the color of the phosphoric acid product (FIPR 2003a). Organic carbon is therefore not included in the calculation of CO<sub>2</sub> emissions from phosphoric acid production. However, if, for example, 50 percent of the organic carbon content of the phosphate rock were to be emitted as CO<sub>2</sub> in the phosphoric acid production process, the CO<sub>2</sub> emission estimate would increase by on the order of 50 percent.

A third source of uncertainty is the assumption that all domestically-produced phosphate rock is used in phosphoric acid production and used without first being calcined. Calcination of the phosphate rock would result in conversion of some of the organic carbon in the phosphate rock into CO<sub>2</sub>. However, according to the USGS, only one producer in Idaho is currently calcining phosphate rock, and no data were available concerning the annual production of this single producer (USGS 2005). Total production of phosphate rock in Utah and Idaho combined amounts to approximately 15 percent of total domestic production in 2004 (USGS 2005). If it is assumed that 100 percent of the reported domestic production of phosphate rock for Idaho and Utah was first calcined, and it is assumed that 50 percent of the organic carbon content of the total production for Idaho and Utah was

converted to CO<sub>2</sub> in the calcination process, the CO<sub>2</sub> emission estimate would increase on the order of 10 percent.

Finally, USGS indicated that 10 percent of domestically-produced phosphate rock is used to manufacture elemental phosphorus and other phosphorus-based chemicals, rather than phosphoric acid (USGS 2004). According to USGS, there is only one domestic producer of elemental phosphorus, in Idaho, and no data were available concerning the annual production of this single producer. Elemental phosphorus is produced by reducing phosphate rock with coal coke, and it is therefore assumed that 100 percent of the carbonate content of the phosphate rock will be converted to CO<sub>2</sub> in the elemental phosphorus production process. The calculation for CO<sub>2</sub> emissions is based on the assumption that phosphate rock consumption, for purposes other than phosphoric acid production, results in CO<sub>2</sub> emissions from 100 percent of the inorganic carbon content in phosphate rock, but none from the organic carbon content. This phosphate rock, consumed for other purposes, constitutes approximately 10 percent of total phosphate rock consumption. If it were assumed that there are zero emissions from other uses of phosphate rock, CO<sub>2</sub> emissions would fall 10 percent.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-35. Phosphoric acid production CO<sub>2</sub> emissions were estimated to be between 1.1 and 1.7 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 18 percent below and 19 percent above the emission estimate of 1.4 Tg CO<sub>2</sub> Eq.

## Planned Improvements

The estimate of CO<sub>2</sub> emissions from phosphoric acid production could be improved through collection of

**Table 4-35: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Phosphoric Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Phosphoric Acid Production	CO <sub>2</sub>	1.4	1.1	1.7	-18%	+19%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



additional data. Additional data is being collected concerning the carbonate content of uncalcined phosphate rock mined in various locations in the United States. Additional research will also be conducted concerning the disposition of the organic carbon content of the phosphate rock in the phosphoric acid production process. Only a single producer of phosphate rock is calcining the product, and only a single producer is manufacturing elemental phosphorus. Annual production data for these single producers will probably remain unavailable.

## 4.9. Ferroalloy Production (IPCC Source Category 2C2)

CO<sub>2</sub> is emitted from the production of several ferroalloys. Ferroalloys are composites of iron and other elements such as silicon, manganese, and chromium. When incorporated in alloy steels, ferroalloys are used to alter the material properties of the steel. Estimates from two types of ferrosilicon (25 to 55 percent and 56 to 95 percent silicon), silicon metal (about 98 percent silicon), and miscellaneous alloys (36 to 65 percent silicon) have been calculated. Emissions from the production of ferrochromium and ferromanganese are not included here because of the small number of manufacturers of these materials in the United States. Subsequently, government information disclosure rules prevent the publication of production data for these production facilities. Similar to emissions from the production of iron and steel, CO<sub>2</sub> is emitted when metallurgical coke is oxidized during a high-temperature reaction with iron and the selected alloying element. Due to

the strong reducing environment, CO is initially produced, and eventually oxidized to CO<sub>2</sub>. A representative reaction equation for the production of 50 percent ferrosilicon is given below:



Emissions of CO<sub>2</sub> from ferroalloy production in 2004 were 1.3 Tg CO<sub>2</sub> Eq. (1,287 Gg) (see Table 4-36), an 11 percent increase from the previous year and a 35 percent reduction since 1990.

## Methodology

Emissions of CO<sub>2</sub> from ferroalloy production were calculated by multiplying annual ferroalloy production by material-specific emission factors. Emission factors taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997) were applied to ferroalloy production. For ferrosilicon alloys containing 25 to 55 percent silicon and miscellaneous alloys (including primarily magnesium-ferrosilicon, but also including other silicon alloys) containing 32 to 65 percent silicon, an emission factor for 50 percent silicon ferrosilicon (2.35 tons CO<sub>2</sub>/ton of alloy produced) was applied. Additionally, for ferrosilicon alloys containing 56 to 95 percent silicon, an emission factor for 75 percent silicon ferrosilicon (3.9 tons CO<sub>2</sub> per ton alloy produced) was applied. The emission factor for silicon metal was assumed to be 4.3 tons CO<sub>2</sub>/ton metal produced. It was assumed that 100 percent of the ferroalloy production was produced using petroleum coke using an electric arc furnace process (IPCC/UNEP/OECD/IEA 1997), although some ferroalloys may have been produced with coking coal, wood, other biomass, or graphite carbon inputs. The amount of petroleum coke consumed in ferroalloy production was calculated assuming that the petroleum coke used is 90 percent carbon and 10 percent inert material.

**Table 4-36: CO<sub>2</sub> Emissions from Ferroalloy Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	2.0	1,980
1998	2.0	2,027
1999	2.0	1,996
2000	1.7	1,719
2001	1.3	1,329
2002	1.2	1,237
2003	1.2	1,159
2004	1.3	1,287

Ferroalloy production data for 1990 through 2004 (see Table 4-37) were obtained from the USGS through personal communications with the USGS Silicon Commodity Specialist (Corathers 2005) and through the *Minerals Yearbook: Silicon Annual Report* (USGS 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004). Until 1999, the USGS reported production of ferrosilicon containing 25 to 55 percent silicon separately from production of miscellaneous alloys containing 32 to 65 percent silicon; beginning in 1999, the USGS reported these as a single category (see Table 4-37).

**Table 4-37: Production of Ferroalloys (Metric Tons)**

Year	Ferrosilicon 25%-55%	Ferrosilicon 56%-95%	Silicon Metal	Misc. Alloys 32-65%
1990	321,385	109,566	145,744	72,442
1998	162,000	147,000	195,000	99,800
1999	252,000	145,000	195,000	NA
2000	229,000	100,000	184,000	NA
2001	167,000	89,000	137,000	NA
2002	156,000	98,000	113,000	NA
2003	113,000	75,800	139,000	NA
2004	120,000	92,300	150,000	NA

NA (Not Available)

The composition data for petroleum coke was obtained from Onder and Bagdoyan (1993).

## Uncertainty

Although some ferroalloys may be produced using wood or other biomass as a carbon source, information and data regarding these practices were not available. Emissions from ferroalloys produced with wood or other biomass would not be counted under this source because wood-based carbon is of biogenic origin.<sup>10</sup> Even though emissions from ferroalloys produced with coking coal or graphite inputs would be counted in national trends, they may be generated with varying amounts of CO<sub>2</sub> per unit of ferroalloy produced. The most accurate method for these estimates would be to base calculations on the amount of reducing agent used in the process, rather than the amount of ferroalloys produced. These data, however, were not available.

Also, annual ferroalloy production is now reported by the USGS in three broad categories: ferroalloys containing 25 to 55 percent silicon (including miscellaneous alloys),

ferroalloys containing 56 to 95 percent silicon, and silicon metal. It was assumed that the IPCC emission factors apply to all of the ferroalloy production processes, including miscellaneous alloys. Finally, production data for silvery pig iron (alloys containing less than 25 percent silicon) are not reported by the USGS to avoid disclosing company proprietary data. Emissions from this production category, therefore, were not estimated.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-38. Ferroalloy production CO<sub>2</sub> emissions were estimated to be between 1.3 and 1.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 3 percent below and 3 percent above the emission estimate of 1.3 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

Estimates of CO<sub>2</sub> emissions from ferroalloy production for 2003 were revised to reflect updated data from the USGS. This change resulted in a decrease in CO<sub>2</sub> emissions from

**Table 4-38: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Ferroalloy Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Ferroalloy Production	CO <sub>2</sub>	1.3	1.3	1.3	-3%	+3%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

<sup>10</sup> Emissions and sinks of biogenic carbon are accounted for in the Land Use, Land-Use Change, and Forestry chapter.

ferroalloy production of 0.2 Tg CO<sub>2</sub> Eq. (16 percent) for 2003.

## 4.10. Carbon Dioxide Consumption (IPCC Source Category 2B5)

CO<sub>2</sub> is used for a variety of commercial applications, including food processing, chemical production, carbonated beverage production, and refrigeration, and is also used in petroleum production for enhanced oil recovery (EOR). CO<sub>2</sub> used for EOR is injected into the underground reservoirs to increase the reservoir pressure to enable additional petroleum to be produced.

For the most part, CO<sub>2</sub> used in non-EOR applications will eventually be released to the atmosphere, and for the purposes of this analysis CO<sub>2</sub> used in commercial applications other than EOR is assumed to be emitted to the atmosphere. CO<sub>2</sub> used in EOR applications is considered for the purposes of this analysis to remain sequestered in the underground formations into which the CO<sub>2</sub> is injected.

It is unclear to what extent the CO<sub>2</sub> used for EOR will be re-released to the atmosphere. CO<sub>2</sub> used in EOR applications is compressed at the CO<sub>2</sub> production source, transported by pipeline to the EOR field, and injected into wellheads. Potential CO<sub>2</sub> leakage pathways from CO<sub>2</sub> production, transportation, and injection include fugitive emissions from the compressors, pipeline equipment, and wellheads. Also, the CO<sub>2</sub> used for EOR may migrate to the wellhead after a few years of injection (Hangebrauk et al. 1992) or may be partially recovered as a component of crude oil produced from the wells (Denbury Resources 2003a). This CO<sub>2</sub> may be recovered and re-injected into the wellhead or separated from the petroleum produced and vented to the atmosphere. More research is required to determine the amount of CO<sub>2</sub> that may escape from EOR operations through leakage from equipment, as a component of the crude oil produced, or as leakage directly from the reservoir through geologic faults and fractures or through improperly plugged or improperly completed wells. For the purposes of this analysis, it is

assumed that all of the CO<sub>2</sub> produced for use in EOR applications is injected into reservoirs (i.e., there is no loss of CO<sub>2</sub> to the atmosphere during CO<sub>2</sub> production, transportation, or injection for EOR applications) and that all of the injected CO<sub>2</sub> remains sequestered within the reservoirs.

CO<sub>2</sub> is produced from naturally occurring CO<sub>2</sub> reservoirs, as a by-product from the energy and industrial production processes (e.g., ammonia production, fossil fuel combustion, ethanol production), and as a by-product from the production of crude oil and natural gas, which contain naturally occurring CO<sub>2</sub> as a component. CO<sub>2</sub> produced from naturally occurring CO<sub>2</sub> reservoirs and used in industrial applications other than EOR is included in this analysis. Neither by-product CO<sub>2</sub> generated from energy or industrial production processes nor CO<sub>2</sub> separated from crude oil and natural gas are included in this analysis for a number of reasons.

Depending on the raw materials that are used, by-product CO<sub>2</sub> generated during energy and industrial production processes may already be accounted for in the CO<sub>2</sub> emission estimates from fossil fuel consumption (either from fossil fuel combustion or from non-energy uses of fossil fuels). For example, ammonia is primarily manufactured using natural gas as both a feedstock and energy source. CO<sub>2</sub> emissions from natural gas combustion for ammonia production are accounted for in the CO<sub>2</sub> from Fossil Fuel Combustion source category of the Energy sector and, therefore, are not included under CO<sub>2</sub> Consumption. Likewise, CO<sub>2</sub> emissions from natural gas used as feedstock for ammonia production are accounted for in this chapter under the Ammonia Manufacture source category and, therefore, are not included here.<sup>11</sup>

CO<sub>2</sub> is produced as a by-product of crude oil and natural gas production. This CO<sub>2</sub> is separated from the crude oil and natural gas using gas processing equipment, and may be emitted directly to the atmosphere, or captured and reinjected into underground formations, used for EOR, or sold for other commercial uses. The amount of CO<sub>2</sub> separated from crude oil and natural gas has not been estimated.<sup>12</sup> Therefore, the only CO<sub>2</sub> consumption that is accounted for in this analysis

<sup>11</sup> One ammonia manufacturer located in Oklahoma is reportedly capturing approximately 35 MMCF/day (0.67 Tg/yr) of by-product CO<sub>2</sub> for use in EOR applications. According to the methodology used in this analysis, this amount of CO<sub>2</sub> would be considered to be sequestered and not emitted to the atmosphere. However, time series data for the amount of CO<sub>2</sub> captured from the ammonia plant for use in EOR applications are not available, and therefore all of the CO<sub>2</sub> produced by the ammonia plant is assumed to be emitted to the atmosphere and is accounted for in this chapter under Ammonia Manufacture.

<sup>12</sup> The United States is in the process of developing a methodology to account for CO<sub>2</sub> emissions from natural gas systems and petroleum systems for inclusion in future Inventory submissions. For more information see Annex 5.

is CO<sub>2</sub> produced from natural wells other than crude oil and natural gas wells that is used in commercial applications other than EOR.

There are currently two facilities, one in Mississippi and one in New Mexico, producing CO<sub>2</sub> from natural CO<sub>2</sub> reservoirs for use in both EOR and in other commercial applications (e.g., chemical manufacturing, food production). There are other naturally occurring CO<sub>2</sub> reservoirs, mostly located in the western U.S. Facilities are producing CO<sub>2</sub> from these natural reservoirs, but they are only producing CO<sub>2</sub> for EOR applications, not for other commercial applications (Allis et al. 2000). In 2004, the amount of CO<sub>2</sub> produced by the Mississippi and New Mexico facilities for commercial applications and subsequently emitted to the atmosphere were 1.2 Tg CO<sub>2</sub> Eq. (1,183 Gg) (see Table 4-39). This amount represents a decrease of 9 percent from the previous year and an increase of 29 percent from emissions in 1990. This increase was due to an increase in the Mississippi facility's reported production for use in other commercial applications.

## Methodology

CO<sub>2</sub> emission estimates for 2001 through 2004 were based on production data for the two facilities currently producing CO<sub>2</sub> from naturally-occurring CO<sub>2</sub> reservoirs. Some of the CO<sub>2</sub> produced by these facilities is used for EOR and some is used in other commercial applications (e.g., chemical manufacturing, food production). CO<sub>2</sub> produced from these two facilities that was used for EOR is assumed to remain sequestered and is not included in the CO<sub>2</sub> emissions totals. It is assumed that 100 percent of the CO<sub>2</sub> production used in commercial applications other than EOR is eventually released into the atmosphere.

**Table 4-39: CO<sub>2</sub> Emissions from CO<sub>2</sub> Consumption (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	0.9	860
1998	0.9	912
1999	0.8	849
2000	1.0	957
2001	0.8	818
2002	1.0	968
2003	1.3	1,293
2004	1.2	1,183

CO<sub>2</sub> production data for the Jackson Dome, Mississippi facility for 2001 through 2004 and the percentage of total production that was used for EOR and in non-EOR applications were obtained from the Annual Reports for Denbury Resources, the operator of the facility (Denbury Resources 2002, 2003b, 2004, 2005). Denbury Resources reported the average CO<sub>2</sub> production in units of MMCF CO<sub>2</sub> per day for 2001 through 2004 and reported the percentage of the total average annual production that was used for EOR. CO<sub>2</sub> production data for the Bravo Dome, New Mexico facility were obtained from the New Mexico Bureau of Geology and Mineral Resources for the years 1990 through 2003 (Broadhead 2005). According to the New Mexico Bureau, the amount of CO<sub>2</sub> produced from Bravo Dome for use in non-EOR applications is less than one percent of total production (Broadhead 2003a). Production data for 2004 were not available for Bravo Dome, so it is assumed that the production values for those years are equal to the 2003 value.

Denbury Resources acquired the Jackson Dome facility in 2001 and CO<sub>2</sub> production data for the Jackson Dome facility are not available for years prior to 2001. Therefore, for 1990 through 2000, CO<sub>2</sub> emissions from CO<sub>2</sub> consumption in commercial applications other than EOR are estimated based on the total annual domestic consumption of CO<sub>2</sub> in commercial applications other than EOR in 2001 multiplied by the percentage of the total CO<sub>2</sub> consumed in commercial applications other than EOR that originated from CO<sub>2</sub> production at the Jackson Dome and Bravo Dome facilities in 2001. The same procedure was followed in 2002, 2003, and 2004 with updated annual data. The total domestic commercial consumption of CO<sub>2</sub> in commercial applications other than EOR as reported by the U.S. Census Bureau was about 13,542 thousand metric tons in 2004. The total non-EOR CO<sub>2</sub> produced from the Jackson Dome and Bravo Dome natural reservoirs in 2004 was about 1,183 thousand metric tons, corresponding to 8.7 percent of the total domestic non-EOR commercial CO<sub>2</sub> consumption. The remaining 91.3 percent of the total annual non-EOR commercial CO<sub>2</sub> consumption is assumed to be accounted for in the CO<sub>2</sub> emission estimates from other categories (e.g., Ammonia Manufacture, CO<sub>2</sub> from Fossil Fuel Combustion, Wood Biomass and Ethanol Consumption).

Non-EOR commercial CO<sub>2</sub> consumption data (see Table 4-40) for years 1991 and 1992 were obtained from *Industry*

**Table 4-40: CO<sub>2</sub> Consumption (Metric Tons)**

Year	Metric Tons
1990	11,997,726
1998	12,716,070
1999	11,843,386
2000	13,354,262
2001	11,413,889
2002	11,313,478
2003	11,165,324
2004	13,542,492

*Report 1992* (U.S. Census 1993). Consumption data are not available for 1990, and therefore CO<sub>2</sub> consumption data for 1990 is assumed to be equal to that for 1991. Consumption data for 1993 and 1994 were obtained from *U.S. Census Bureau Manufacturing Profile, 1994* (U.S. Census 1995). Consumption data for 1996 through 2004 were obtained from the U.S. Census Bureau's *Industry Report, 1996, 1998, 2000, 2002, 2003, 2004* (U.S. Census 1997, 1999, 2001, 2003, 2004, 2005).

## Uncertainty

Uncertainty is associated with the number of facilities that are currently producing CO<sub>2</sub> from naturally occurring reservoirs for commercial uses other than EOR, and for which the CO<sub>2</sub> emissions are not accounted for elsewhere. Research indicates that there are only two such facilities, which are in New Mexico and Mississippi, however, additional facilities may exist that have not been identified. In addition, it is possible that CO<sub>2</sub> recovery exists in particular production and end-use sectors that are not accounted for elsewhere. Such recovery may or may not affect the overall estimate of CO<sub>2</sub> emissions from that sector depending upon the end use to which the recovered CO<sub>2</sub> is applied. For example, research has identified one ammonia production facility that is recovering CO<sub>2</sub> for use

in EOR. Such CO<sub>2</sub> would be assumed to remain sequestered; however, time series data for the amount of recovered is not available and therefore all of the CO<sub>2</sub> produced by this plant is assumed to be emitted to the atmosphere and is allocated to Ammonia Manufacture. Recovery of CO<sub>2</sub> from ammonia production facilities for use in EOR is further discussed in this chapter under Ammonia Manufacture. Further research is required to determine whether CO<sub>2</sub> is being recovered from other facilities for application to end uses that are not accounted for elsewhere.

There is also uncertainty associated with the assumption that 100 percent of the CO<sub>2</sub> used for EOR is sequestered. Operating experience with EOR systems indicates that 100 percent of the CO<sub>2</sub> used in EOR applications does not remain sequestered, but rather that it may be emitted to the atmosphere as leakage from equipment and reservoirs or recovered as a component of the crude oil produced. Potential sources of CO<sub>2</sub> emissions from EOR applications include leakage from equipment used to produce, transport, compress, and inject the CO<sub>2</sub>, leakage from equipment used to process the crude oil produced, separate the CO<sub>2</sub> from the crude oil and recompress and recycle (reinject) the CO<sub>2</sub> recovered from the crude oil. Other potential sources of CO<sub>2</sub> emissions from EOR applications include leakage from the reservoir itself, either through migration of the injected CO<sub>2</sub> beyond the boundaries of the reservoir, chemical interactions between the injected CO<sub>2</sub> and the reservoir rock, and leakage via faults, fractures, oil and gas well bores, and water wells.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-41. CO<sub>2</sub> consumption CO<sub>2</sub> emissions were estimated to be between 1.0 and 1.4 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 14 percent below to 14 percent above the emission estimate of 1.2 Tg CO<sub>2</sub> Eq.

**Table 4-41: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from CO<sub>2</sub> Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
CO <sub>2</sub> Consumption	CO <sub>2</sub>	1.2	1.0	1.4	-14%	+14%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



# Recalculations Discussion

Total CO<sub>2</sub> consumption values were updated for 2003, as was CO<sub>2</sub> production for Jackson Dome, based on revised data in the Census Bureau’s Industry Reports and Denbury Resources’ Annual Report, respectively. Data for the Bravo Dome were updated for the entire time series based on new production data from the facility. For Jackson Dome, revised 2003 production data resulted in a 33 percent increase in emissions from the previous estimate. For Jackson Dome, updated production data resulted in an approximate emissions decrease of 1 percent for 2001, 17 percent for 2002, and 11 percent for 2003. Revisions to the datasets resulted in a 1 percent decrease in CO<sub>2</sub> emissions from CO<sub>2</sub> consumption in 2002 and a 2 percent increase in CO<sub>2</sub> emissions from CO<sub>2</sub> consumption in 2003 relative to data published in the previous Inventory.

## 4.11. Zinc Production

Zinc production in the United States consists of both primary and secondary processes. Primary production techniques used in the United States are the electro-thermic and electrolytic process while secondary techniques used in the United States include a range of metallurgical, hydrometallurgical, and pyrometallurgical processes. Worldwide primary zinc production also employs a pyrometallurgical process using the Imperial Smelting Furnace process; however, this process is not used in the United States (Sjardin 2003). Of the primary and secondary processes used in the United States, the electro-thermic process results in non-energy CO<sub>2</sub> emissions, as does the Waelz Kiln process—a technique used to produce secondary zinc from electric-arc furnace (EAF) dust (Viklund-White 2000). Total zinc production has decreased by 15 percent in the United States since 1990 while world production has increased by 38 percent over this same period (USGS 1995, 2004).

During the electro-thermic zinc production process, roasted zinc concentrate and, when available, secondary zinc products enter a sinter feed where they are burned to remove impurities before entering an electric retort furnace. Metallurgical coke added to the electric retort furnace reduces the zinc oxides and produces vaporized zinc, which is then captured in a vacuum condenser. This reduction process produces non-energy CO<sub>2</sub> emissions (Sjardin 2003). The

electrolytic zinc production process does not produce non-energy CO<sub>2</sub> emissions.

In the Waelz Kiln process, EAF dust, which is captured during the recycling of galvanized steel, enters a kiln along with a reducing agent—often metallurgical coke. When kiln temperatures reach approximately 1100-1200°C, zinc fumes are produced, which are combusted with air entering the kiln. This combustion forms zinc oxide, which is collected in a baghouse or electrostatic precipitator, and is then leached to remove chloride and fluoride. Through this process, approximately 0.33 tons of zinc are produced for every ton of EAF dust treated (Viklund-White 2000).

In 2004, U.S. primary and secondary zinc production totaled 567,900 metric tons (USGS 2004). The resulting emissions of CO<sub>2</sub> from zinc production in 2004 were estimated to be 0.5 Tg CO<sub>2</sub> Eq. (502 Gg) (see Table 4-42). All 2004 CO<sub>2</sub> emissions result from secondary zinc production.

After a gradual increase in total emissions from 1990 to 2000, largely due to an increase in secondary zinc production, 2004 emissions have decreased by nearly half that of 1990 (47 percent) due to the closing of an electro-thermic-process zinc plant in Monaca, PA (USGS 2004).

## Methodology

Non-energy CO<sub>2</sub> emissions from zinc production result from those processes that use metallurgical coke or other carbon-based materials as reductants. Sjardin (2003) provides an emission factor of 0.43 metric tons CO<sub>2</sub>/ton zinc produced for emissive zinc production processes; however, this emission factor is based on the Imperial Smelting Furnace production process. Because the Imperial Smelting Furnace production process is not used in the United States,

**Table 4-42: CO<sub>2</sub> Emissions from Zinc Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	0.9	939
1998	1.1	1,140
1999	1.1	1,080
2000	1.1	1,129
2001	1.0	976
2002	0.9	927
2003	0.5	502
2004	0.5	502



emission factors specific to those emissive zinc production processes used in the United States, which consist of the electro-thermic and Waelz Kiln processes, were needed. Due to the limited amount of information available for these electro-thermic processes, only Waelz Kiln process-specific emission factors were developed. These emission factors were applied to both the Waelz Kiln process and the electro-thermic zinc production processes. A Waelz Kiln emission factor based on the amount of zinc produced was developed based on the amount of metallurgical coke consumed for non-energy purposes per ton of zinc produced, 1.19 metric tons coke/metric ton zinc produced (Viklund-White 2000), and the following equation:

$$EF_{\text{Waelz Kiln}} = \frac{1.19 \text{ metric tons coke}}{\text{metric tons zinc}} \times \frac{0.84 \text{ metric tons C}}{\text{metric ton coke}} \times \frac{3.67 \text{ metric tons CO}_2}{\text{metric ton C}} \times \frac{1.23 \text{ metric tons CO}_2}{\text{metric ton zinc}}$$

The USGS disaggregates total U.S. primary zinc production capacity into zinc produced using the electro-thermic process and zinc produced using the electrolytic process; however, the USGS does not report the amount of zinc produced using each process, only the total zinc production capacity of the zinc plants using each process. The total electro-thermic zinc production capacity is divided by total primary zinc production capacity to estimate the percent of primary zinc produced using the electro-thermic process. This percent is then multiplied by total primary zinc production to estimate the amount of zinc produced using the electro-thermic process, and the resulting value is multiplied by the Waelz Kiln process emission factor to obtain total CO<sub>2</sub> emissions for primary zinc production. According to the USGS, the only remaining plant producing primary zinc using the electro-thermic process closed in 2003 (USGS 2004). Therefore, CO<sub>2</sub> emissions for primary zinc production are reported only for years 1990 through 2002.

In the United States, secondary zinc is produced through either the electro-thermic or Waelz Kiln process. In 1997, the Horsehead Corporation plant, located in Monaca, PA, produced 47,174 metric tons of secondary zinc using the

electro-thermic process (Queneau et al. 1998). This is the only plant in the United States that uses the electro-thermic process to produce secondary zinc, which, in 1997, accounted for 13 percent of total secondary zinc production. This percentage was applied to all years within the time series up until the Monaca plant's closure in 2003 (USGS 2004) to estimate the total amount of secondary zinc produced using the electro-thermic process. This value is then multiplied by the Waelz Kiln process emission factor to obtain total CO<sub>2</sub> emissions for secondary zinc produced using the electro-thermic process.

U.S. secondary zinc is also produced by processing recycled EAF dust in a Waelz Kiln furnace. Due to the complexities of recovering zinc from recycled EAF dust, an emission factor based on the amount of EAF dust consumed rather than the amount of secondary zinc produced is believed to represent actual CO<sub>2</sub> emissions from the process more accurately (Stuart 2005). An emission factor based on the amount of EAF dust consumed was developed based on the amount of metallurgical coke consumed per ton of EAF dust consumed, 0.4 metric tons coke/metric ton EAF dust consumed (Viklund-White 2000), and the following equation:

$$EF_{\text{EAF Dust}} = \frac{0.4 \text{ metric tons coke}}{\text{metric tons EAF dust}} \times \frac{0.84 \text{ metric tons C}}{\text{metric ton coke}} \times \frac{3.67 \text{ metric tons CO}_2}{\text{metric ton C}} \times \frac{1.23 \text{ metric tons CO}_2}{\text{metric ton EAF dust}}$$

The Horsehead Corporation plant, located in Palmerton, PA, is the only large plant in the United States that produces secondary zinc by recycling EAF dust (Stuart 2005). In 2003, this plant consumed 408,240 metric tons of EAF dust, producing 137,169 metric tons of secondary zinc (Recycling Today 2005). This zinc production accounted for 36 percent of total secondary zinc produced in 2003. This percentage was applied to the USGS data for total secondary zinc production for all years within the time series to estimate the total amount of secondary zinc produced by consuming recycled EAF dust in a Waelz Kiln furnace. This value is multiplied by the Waelz Kiln process emission factor for EAF dust to obtain total CO<sub>2</sub> emissions.

**Table 4-43: Zinc Production (Metric Tons)**

Year	Primary	Secondary
1990	262,704	341,400
1991	253,282	351,457
1992	271,867	365,623
1993	240,000	358,000
1994	216,600	361,000
1995	231,840	353,000
1996	225,400	378,000
1997	226,700	374,000
1998	233,900	426,000
1999	241,100	398,000
2000	227,800	440,000
2001	203,000	375,000
2002	181,800	366,000
2003	186,900	381,000
2004	186,900	381,000

The 1990 through 2003 activity data for primary and secondary zinc production (see Table 4-43) were obtained through the USGS *Mineral Yearbook: Zinc* (USGS 1994, 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004). Because data for 2004 are not yet available, 2004 data are assumed to equal 2003 data.

## Uncertainty

The uncertainties contained in these estimates are two-fold, relating to activity data and emission factors used.

First, there are uncertainties associated with the percent of total zinc production, both primary and secondary, that is attributed to the electro-thermic and Waelz Kiln emissive zinc production processes. For primary zinc production, the amount of zinc produced annually using the electro-thermic process is estimated from the percent of primary-zinc production capacity that electro-thermic production capacity constitutes for each year of the time series. This assumes that each zinc plant is operating at the same percentage of total production capacity, which may not be the case and

this calculation could either overestimate or underestimate the percentage of the total primary zinc production that is produced using the electro-thermic process. The amount of secondary zinc produced using the electro-thermic process is estimated from the percent of total secondary zinc production that this process accounted for during a single year, 2003. The amount of secondary zinc produced using the Waelz Kiln process is estimated from the percent of total secondary zinc production this process accounted for during a single year, 1997. This calculation could either overestimate or underestimate the percentage of the total secondary zinc production that is produced using the electro-thermic or Waelz Kiln processes. Therefore, there is uncertainty associated with the fact that percents of total production data estimated from production capacity, rather than actual production data, are used for emission estimates.

Second, there are uncertainties associated with the emission factors used to estimate CO<sub>2</sub> emissions from the primary and secondary production processes. Because the only published emission factors are based on the Imperial Smelting Furnace, which is not used in the United States, country-specific emission factors were developed for the Waelz Kiln zinc production process. Data limitations prevented the development of emission factors for the electro-thermic process. Therefore, emission factors for the Waelz Kiln process were applied to both electro-thermic and Waelz Kiln production processes. Furthermore, the Waelz Kiln emission factors are based on materials balances for metallurgical coke and EAF dust consumed during zinc production provided by Viklund-White (2000). Therefore, the accuracy of these emission factors depend upon the accuracy of these materials balances.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-44. Zinc production CO<sub>2</sub> emissions were estimated to be between 0.4 and 0.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out

**Table 4-44: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Zinc Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Zinc Production	CO <sub>2</sub>	0.5	0.4	0.6	-12%	+13%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 12 percent below and 13 percent above the emission estimate of 0.5 Tg CO<sub>2</sub> Eq.

## 4.12. Lead Production

Lead production in the United States consists of both primary and secondary processes. In the United States, primary lead production, in the form of direct smelting, mostly occurs at a plant located in Missouri, while secondary production largely involves the recycling of lead acid batteries at 15 separate smelters located in 11 states throughout the United States (USGS 2004). Secondary lead production has increased in the United States over the past decade while primary lead production has decreased, to where 2004 secondary lead production accounted for approximately 88 percent of total lead production (USGS 1995, 2004). Both the primary lead and secondary lead production processes used in the United States emit CO<sub>2</sub> (Sjardin 2003).

Primary production of lead through the direct smelting of lead concentrate produces CO<sub>2</sub> emissions as the lead concentrates are reduced in a furnace using metallurgical coke (Sjardin 2003). U.S. primary lead production decreased by 40 percent from 2003 to 2004 due to the closing of one of two primary lead production plants in Missouri and has decreased by 63 percent since 1990 (USGS 1995, Gabby 2005).

In the United States, approximately 82 percent of secondary lead is produced by recycling lead acid batteries in either blast furnaces or reverberatory furnaces. The remaining 18 percent of secondary lead is produced from lead scrap. Similar to primary lead production, CO<sub>2</sub> emissions result when a reducing agent, usually metallurgical coke, is added to the smelter to aid in the reduction process (Sjardin 2003). U.S. secondary lead production decreased by 3 percent from 2003 to 2004, but has increased by 17 percent since 1990.

In 2004, U.S. primary and secondary lead production totaled 1,258,00 metric tons (USGS 2004). The resulting emissions of CO<sub>2</sub> from 2004 production were estimated to be 0.3 Tg CO<sub>2</sub> Eq. (259 Gg) (see Table 4-45). The majority of 2004 lead production is from secondary processes, which account for 85 percent of total 2004 CO<sub>2</sub> emissions.

After a gradual increase in total emissions from 1990 to 2000, total emissions have decreased by nine percent since 1990, largely due a decrease in primary production

and a transition within the United States from primary lead production to secondary lead production, which is less emissive than primary production (USGS 2004).

## Methodology

Non-energy CO<sub>2</sub> emissions from lead production result from primary and secondary production processes that use metallurgical coke or other carbon-based materials as reductants. For primary lead production using direct smelting, Sjardin (2003) provides an emission factor of 0.25 metric tons CO<sub>2</sub>/ton lead. For secondary lead production, Sjardin (2003) provides an emission factor of 0.2 metric tons CO<sub>2</sub>/ton lead produced. Both factors are multiplied by total U.S. primary and secondary lead production, respectively, to estimate CO<sub>2</sub> emissions.

The 1990 through 2003 activity data for primary and secondary lead production (see Table 4-46) were obtained through the USGS *Mineral Yearbook: Lead* (USGS 1994,

**Table 4-45: CO<sub>2</sub> Emissions from Lead Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	0.3	285
1998	0.3	308
1999	0.3	310
2000	0.3	311
2001	0.3	293
2002	0.3	290
2003	0.3	289
2004	0.3	259

**Table 4-46: Lead Production (Metric Tons)**

Year	Primary	Secondary
1990	404,000	922,000
1991	345,900	885,000
1992	304,800	916,000
1993	334,900	893,000
1994	351,400	931,000
1995	374,000	1,020,000
1996	326,000	1,070,000
1997	343,000	1,110,000
1998	337,000	1,120,000
1999	350,000	1,110,000
2000	341,000	1,130,000
2001	290,000	1,100,000
2002	262,000	1,120,000
2003	245,000	1,140,000
2004	148,000	1,110,000

**Table 4-47: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> Emissions from Lead Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Lead Production	CO <sub>2</sub>	0.3	0.2	0.3	-11%	+11%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002, 2003, 2004). Primary and secondary lead production data for 2004 were obtained from the USGS Lead Minerals Commodity Specialist (Gabby 2005).

## Uncertainty

Uncertainty associated with lead production relates to the emission factors and activity data used. The direct smelting emission factor used in primary production is taken from Sjardin (2003) who averages the values provided by three other studies (Dutrizac et al. 2000, Morris et al. 1983, Ullman 1997). For secondary production, Sjardin (2003) reduces this factor by 50 percent and adds a CO<sub>2</sub> emissions factor associated with battery treatment. The applicability of these emission factors to plants in the United States is uncertain. There is also a smaller level of uncertainty associated with the accuracy of primary and secondary production data provided by the USGS.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-47. Lead production CO<sub>2</sub> emissions were estimated to be between 0.2 and 0.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 11 percent below and 11 percent above the emission estimate of 0.3 Tg CO<sub>2</sub> Eq.

## 4.13. Petrochemical Production (IPCC Source Category 2B5)

The production of some petrochemicals results in the release of small amounts of CH<sub>4</sub> and CO<sub>2</sub> emissions. Petrochemicals are chemicals isolated or derived from petroleum or natural gas. CH<sub>4</sub> emissions are presented here from the production of carbon black, ethylene, ethylene dichloride, styrene, and methanol, while CO<sub>2</sub> emissions are presented here for only carbon black production. The CO<sub>2</sub>

emissions from petrochemical processes other than carbon black are currently included in the Carbon Stored in Products from Non-Energy Uses of Fossil Fuels Section of the Energy chapter. The CO<sub>2</sub> from carbon black production is included here to allow for the direct reporting of CO<sub>2</sub> emissions from the process and direct accounting of the feedstocks used in the process.

Carbon black is an intensely black powder generated by the incomplete combustion of an aromatic petroleum or coal-based feedstock. Most carbon black produced in the United States is added to rubber to impart strength and abrasion resistance, and the tire industry is by far the largest consumer. Ethylene is consumed in the production processes of the plastics industry including polymers such as high, low, and linear low density polyethylene (HDPE, LDPE, LLDPE), polyvinyl chloride (PVC), ethylene dichloride, ethylene oxide, and ethylbenzene. Ethylene dichloride is one of the first manufactured chlorinated hydrocarbons with reported production as early as 1795. In addition to being an important intermediate in the synthesis of chlorinated hydrocarbons, ethylene dichloride is used as an industrial solvent and as a fuel additive. Styrene is a common precursor for many plastics, rubber, and resins. It can be found in many construction products, such as foam insulation, vinyl flooring, and epoxy adhesives. Methanol is an alternative transportation fuel as well as a principle ingredient in windshield wiper fluid, paints, solvents, refrigerants, and disinfectants. In addition, methanol-based acetic acid is used in making PET plastics and polyester fibers.

Emissions of CO<sub>2</sub> and CH<sub>4</sub> from petrochemical production in 2004 were 2.9 Tg CO<sub>2</sub> Eq. (2,895 Gg) and 1.6 Tg CO<sub>2</sub> Eq. (77 Gg), respectively (see Table 4-48 and Table 4-49). Emissions of CO<sub>2</sub> from carbon black production in 2004 increased four percent from the previous year, and there has been an overall increase in CO<sub>2</sub> emissions from carbon black production of 30 percent since 1990. CH<sub>4</sub>

**Table 4-48: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Petrochemical Production (Tg CO<sub>2</sub> Eq.)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	2.2		3.0	3.1	3.0	2.8	2.9	2.8	2.9
CH <sub>4</sub>	1.2		1.7	1.7	1.7	1.4	1.5	1.5	1.6
<b>Total</b>	<b>3.4</b>		<b>4.7</b>	<b>4.8</b>	<b>4.7</b>	<b>4.2</b>	<b>4.4</b>	<b>4.3</b>	<b>4.5</b>

**Table 4-49: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Petrochemical Production (Gg)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	2,221		3,015	3,054	3,004	2,787	2,857	2,777	2,895
CH <sub>4</sub>	56		80	81	80	68	72	72	77

emissions from petrochemical production increased by seven percent from the previous year and increased 38 percent since 1990.

## Methodology

Emissions of CH<sub>4</sub> were calculated by multiplying annual estimates of chemical production by the appropriate emission factor, as follows: 11 kg CH<sub>4</sub>/metric ton carbon black, 1 kg CH<sub>4</sub>/metric ton ethylene, 0.4 kg CH<sub>4</sub>/metric ton ethylene dichloride,<sup>13</sup> 4 kg CH<sub>4</sub>/metric ton styrene, and 2 kg CH<sub>4</sub>/metric ton methanol. Although the production of other chemicals may also result in CH<sub>4</sub> emissions, there were not sufficient data available to estimate their emissions.

Emission factors were taken from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997). Annual production data for 1990 (see Table 4-50) were obtained from the Chemical Manufacturer's Association *Statistical Handbook* (CMA 1999). Production data for 1991 through 2004 were obtained from the American Chemistry Council's *Guide to the Business of Chemistry* (ACC 2002, 2003, 2005)

and the International Carbon Black Association (Johnson 2003, 2005).

Almost all carbon black in the United States is produced from petroleum-based or coal-based feedstocks using the "furnace black" process (European IPPC Bureau 2004). The furnace black process is a partial combustion process in which a portion of the carbon black feedstock is combusted to provide energy to the process. Carbon black is also produced in the United States by the thermal cracking of acetylene-containing feedstocks ("acetylene black process") and by the thermal cracking of other hydrocarbons ("thermal black process"). One U.S. carbon black plant produces carbon black using the thermal black process, and one U.S. carbon black plant produces carbon black using the acetylene black process (The Innovation Group 2004).

The furnace black process produces carbon black from "carbon black feedstock" (also referred to as "carbon black oil"), which is a heavy aromatic oil that may be derived as a byproduct of either the petroleum refining process or the metallurgical (coal) coke production process. For the

**Table 4-50: Production of Selected Petrochemicals (Thousand Metric Tons)**

Chemical	1990		1998	1999	2000	2001	2002	2003	2004
Carbon Black	1,307		1,775	1,798	1,769	1,641	1,682	1,635	1,704
Ethylene	16,542		23,474	25,118	24,971	22,521	23,623	22,957	25,660
Ethylene Dichloride	6,282		11,080	10,308	9,866	9,294	9,288	9,952	12,111
Styrene	3,637		5,183	5,410	5,420	4,277	4,974	5,239	5,468
Methanol	3,785		5,860	5,303	4,876	3,402	3,289	3,166	2,937

<sup>13</sup> The emission factor obtained from IPCC/UNEP/OECD/IEA (1997), page 2.23 is assumed to have a misprint; the chemical identified should be ethylene dichloride (C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) rather than dichloroethylene (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>).



production of both petroleum-derived and coal-derived carbon black, the “primary feedstock” (i.e., carbon black feedstock) is injected into a furnace that is heated by a “secondary feedstock” (generally natural gas). Both the natural gas secondary feedstock and a portion of the carbon black feedstock are oxidized to provide heat to the production process and pyrolyze the remaining carbon black feedstock to carbon black. The “tail gas” from the furnace black process contains CO<sub>2</sub>, carbon monoxide, sulfur compounds, CH<sub>4</sub>, and non-CH<sub>4</sub> volatile organic compounds. A portion of the tail gas is generally burned for energy recovery to heat the downstream carbon black product dryers. The remaining tail gas may also be burned for energy recovery, flared, or vented uncontrolled to the atmosphere.

The calculation of the carbon lost during the production process is the basis for determining the amount of CO<sub>2</sub> released during the process. The carbon content of national carbon black production is subtracted from the total amount of carbon contained in primary and secondary carbon black feedstock to find the amount of carbon lost during the production process. It is assumed that the carbon lost in this process is emitted to the atmosphere as either CH<sub>4</sub> or CO<sub>2</sub>. The carbon content of the CH<sub>4</sub> emissions, estimated as described above, is subtracted from the total carbon lost in the process to calculate the amount of carbon emitted as CO<sub>2</sub>. The total amount of primary and secondary carbon black feedstock consumed in the process (see Table 4-51) is estimated using a primary feedstock consumption factor and a secondary feedstock consumption factor estimated from U.S. Census Bureau (1999 and 2004) data. The average carbon black feedstock consumption factor for U.S. carbon black production is 1.43 metric tons of carbon black feedstock consumed per metric ton of carbon black produced. The average natural gas consumption factor for U.S. carbon black production is 341 normal cubic meters of natural gas consumed per metric ton of carbon black produced. The amount of carbon contained in the primary and secondary feedstocks is calculated by applying the respective

carbon contents of the feedstocks to the respective levels of feedstock consumption.

For the purposes of emissions estimation, 100 percent of the primary carbon black feedstock is assumed to be derived from petroleum refining byproducts. Carbon black feedstock derived from metallurgical (coal) coke production (e.g., creosote oil) is also used for carbon black production; however, no data are available concerning the annual consumption of coal-derived carbon black feedstock. Carbon black feedstock derived from petroleum refining byproducts is assumed to be 89 percent elemental carbon (Srivastava et al. 1999). It is assumed that 100 percent of the tail gas produced from the carbon black production process is combusted and that none of the tail gas is vented to the atmosphere uncontrolled. The furnace black process is assumed to be the only process used for the production of carbon black because of the lack of data concerning the relatively small amount of carbon black produced using the acetylene black and thermal black processes. The carbon black produced from the furnace black process is assumed to be 97 percent elemental carbon (Othmer et al. 1992).

## Uncertainty

The CH<sub>4</sub> emission factors used for petrochemical production are based on a limited number of studies. Using plant-specific factors instead of average factors could increase the accuracy of the emission estimates; however, such data were not available. There may also be other significant sources of CH<sub>4</sub> arising from petrochemical production activities that have not been included in these estimates.

The results of the quantitative uncertainty analysis for the CO<sub>2</sub> emissions from carbon black production calculation are based on feedstock consumption, import and export data, and carbon black production data. The composition of carbon black feedstock varies depending upon the specific refinery production process, and therefore the assumption that carbon black feedstock is 89 percent carbon gives rise to uncertainty.

**Table 4-51: Carbon Black Feedstock (Primary Feedstock) and Natural Gas Feedstock (Secondary Feedstock) Consumption (Thousand Metric Tons)**

Activity	1990	1998	1999	2000	2001	2002	2003	2004
Primary Feedstock	1,864	2,530	2,563	2,521	2,339	2,398	2,331	2,430
Secondary Feedstock	302	410	415	408	379	388	377	393

**Table 4-52: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> Emissions from Petrochemical Production and CO<sub>2</sub> Emissions from Carbon Black Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Petrochemical Production	CH <sub>4</sub>	1.6	1.5	1.7	-8%	+6%
Petrochemical Production	CO <sub>2</sub>	2.9	2.5	3.1	-14%	+5%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

Also, no data are available concerning the consumption of coal-derived carbon black feedstock, so CO<sub>2</sub> emissions from the utilization of coal-based feedstock are not included in the emission estimate. In addition, other data sources indicate that the amount of petroleum-based feedstock used in carbon black production may be underreported by the U.S. Census Bureau. Finally, the amount of carbon black produced from the thermal black process and acetylene black process, although estimated to be a small percentage of the total production, is not known. Therefore, there is some uncertainty associated with the assumption that all of the carbon black is produced using the furnace black process.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-52. Petrochemical production CH<sub>4</sub> emissions were estimated to be between 1.5 and 1.7 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 8 percent below to 6 percent above the emission estimate of 1.6 Tg CO<sub>2</sub> Eq. Petrochemical production CO<sub>2</sub> emissions were estimated to be between 2.5 and 3.1 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or

in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 14 percent below to 5 percent above the emission estimate of 2.9 Tg CO<sub>2</sub> Eq.

## 4.14. Silicon Carbide Production (IPCC Source Category 2B4) and Consumption

CH<sub>4</sub> is emitted from the production of silicon carbide (SiC), a material used as an industrial abrasive; CO<sub>2</sub> is emitted from the use of SiC for metallurgical and other non-abrasive applications. To make SiC, quartz (SiO<sub>2</sub>) is reacted with carbon in the form of petroleum coke. During this reaction, CH<sub>4</sub> is produced from volatile compounds in the petroleum coke. While CO<sub>2</sub> is also emitted from the production process, the requisite data were unavailable for these calculations. CO<sub>2</sub> emissions associated with the use of petroleum coke in the SiC process are accounted for in the Non-Energy Uses of Fossil Fuels section in the Energy Chapter. CH<sub>4</sub> emissions from SiC production in 2004 were 0.4 Gg CH<sub>4</sub> (0.01 Tg CO<sub>2</sub> Eq.) (see Table 4-53 and Table 4-54).

**Table 4-53: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Silicon Carbide Production and Consumption (Tg CO<sub>2</sub> Eq.)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	0.1		0.2	0.1	0.1	0.1	0.1	0.1	0.1
CH <sub>4</sub>	+		+	+	+	+	+	+	+
<b>Total</b>	<b>0.1</b>		<b>0.2</b>	<b>0.2</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>	<b>0.1</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

**Table 4-54: CO<sub>2</sub> and CH<sub>4</sub> Emissions from Silicon Carbide Production and Consumption (Gg)**

Year	1990		1998	1999	2000	2001	2002	2003	2004
CO <sub>2</sub>	100		190	137	130	94	105	111	133
CH <sub>4</sub>	1		1	1	1	+	+	+	+

+ Does not exceed 0.5 Gg.

The USGS reports that a portion (approximately 50 percent) of SiC is used in metallurgical and other non-abrasive applications, primarily in iron and steel production (USGS 2005a). This consumption of SiC produces CO<sub>2</sub> emissions. Considering utilization of both domestically produced SiC and imported SiC in such applications, the amount of CO<sub>2</sub> emitted from SiC consumption in 2004 were 133 Gg CO<sub>2</sub> (0.1 Tg CO<sub>2</sub> Eq.) (see Table 4-53 and Table 4-54).

## Methodology

Emissions of CH<sub>4</sub> were calculated by multiplying annual SiC production by an emission factor (11.6 kg CH<sub>4</sub>/metric ton SiC). This emission factor was derived empirically from measurements taken at Norwegian SiC plants (IPCC/UNEP/OECD/IEA 1997).

Emissions of CO<sub>2</sub> were calculated by multiplying the annual SiC consumption (production plus net imports) by the percent used in metallurgical and other non-abrasive

uses (50 percent) (USGS 2005a). The total SiC consumed in metallurgical and other non-abrasive uses was multiplied by the carbon content of SiC (31.5 percent), which was determined according to the molecular weight ratio of SiC.

Production data for 1990 through 2004 were obtained from the *Minerals Yearbook: Volume I-Metals and Minerals, Manufactured Abrasives* (USGS 1991a, 1992a, 1993a, 1994a, 1995a, 1996a, 1997a, 1998a, 1999a, 2000a, 2001a, 2002a, 2003a, 2004a, 2005a). Silicon carbide consumption by major end use was obtained from the *Minerals Yearbook: Silicon* (USGS 1991b, 1992b, 1993b, 1994b, 1995b, 1996b, 1997b, 1998b, 1999b, 2000b, 2001b, 2002b, 2003b, 2004b, 2005b) (see Table 4-55). Net imports were obtained from the U.S. Census Bureau (2005).

## Uncertainty

The emission factor used for silicon carbide production was based on one study of Norwegian plants. The applicability of this factor to average U.S. practices at silicon carbide plants is uncertain. An alternative would be to calculate emissions based on the quantity of petroleum coke used during the production process rather than on the amount of silicon carbide produced. However, these data were not available. There is also some uncertainty associated with production, net imports, and consumption data as well as the percent of total consumption that is attributed to metallurgical and other non-abrasive uses.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-56. Silicon carbide production CH<sub>4</sub> emissions were estimated to be between 0.0077 and 0.0094 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 10 percent below to 10 percent above the emission estimate of 0.0085 Tg CO<sub>2</sub> Eq.

**Table 4-55: Production and Consumption of Silicon Carbide (Metric Tons)**

Year	Production	Consumption
1990	105,000	172,464
1991	78,900	138,652
1992	84,300	159,902
1993	74,900	173,508
1994	84,700	179,055
1995	75,400	227,397
1996	73,600	240,781
1997	68,200	292,050
1998	69,800	329,040
1999	65,000	237,346
2000	45,000	225,280
2001	40,000	162,142
2002	30,000	180,956
2003	35,000	191,289
2004	35,000	229,693

**Table 4-56: Tier 2 Quantitative Uncertainty Estimates for CH<sub>4</sub> and CO<sub>2</sub> Emissions from Silicon Carbide Production and Consumption (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Silicon Carbide Production	CH <sub>4</sub>	+	+	+	-10%	+10%
Silicon Carbide Consumption	CO <sub>2</sub>	0.1	0.1	0.2	-17%	+18%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq. or 0.5 Gg.

Silicon carbide consumption CO<sub>2</sub> emissions were estimated to be between 0.1 and 0.2 Tg CO<sub>2</sub> Eq. percent confidence level. This indicates a range of approximately 17 percent below to 18 percent above the emission estimate of 0.1 Tg CO<sub>2</sub> Eq.

## 4.15. Nitric Acid Production (IPCC Source Category 2B2)

Nitric acid (HNO<sub>3</sub>) is an inorganic compound used primarily to make synthetic commercial fertilizers. It is also a major component in the production of adipic acid—a feedstock for nylon—and explosives. Virtually all of the nitric acid produced in the United States is manufactured by the catalytic oxidation of ammonia (EPA 1997). During this reaction, N<sub>2</sub>O is formed as a by-product and is released from reactor vents into the atmosphere.

Currently, the nitric acid industry controls for NO and NO<sub>2</sub> (i.e., NO<sub>x</sub>). As such, the industry uses a combination of non-selective catalytic reduction (NSCR) and selective catalytic reduction (SCR) technologies. In the process of destroying NO<sub>x</sub>, NSCR systems are also very effective at destroying N<sub>2</sub>O. However, NSCR units are generally not preferred in modern plants because of high energy costs and associated high gas temperatures. NSCRs were widely installed in nitric plants built between 1971 and 1977. Approximately 20 percent of nitric acid plants use NSCR (Choe et al. 1993). The remaining 80 percent use SCR or extended absorption, neither of which is known to reduce N<sub>2</sub>O emissions.

N<sub>2</sub>O emissions from this source were estimated to be 16.6 Tg CO<sub>2</sub> Eq. (54 Gg) in 2004 (see Table 4-57). Emissions

**Table 4-57: N<sub>2</sub>O Emissions from Nitric Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	17.8	58
1998	20.9	67
1999	20.1	65
2000	19.6	63
2001	15.9	51
2002	17.2	56
2003	16.7	54
2004	16.6	54

from nitric acid production have decreased by 7 percent since 1990, with the trend in the time series closely tracking the changes in production.

## Methodology

N<sub>2</sub>O emissions were calculated by multiplying nitric acid production by the amount of N<sub>2</sub>O emitted per unit of nitric acid produced. The emission factor was determined as a weighted average of 2 kg N<sub>2</sub>O / metric ton HNO<sub>3</sub> for plants using non-selective catalytic reduction (NSCR) systems and 9.5 kg N<sub>2</sub>O / metric ton HNO<sub>3</sub> for plants not equipped with NSCR (Choe et al. 1993). In the process of destroying NO<sub>x</sub>, NSCR systems destroy 80 to 90 percent of the N<sub>2</sub>O, which is accounted for in the emission factor of 2 kg N<sub>2</sub>O / metric ton HNO<sub>3</sub>. An estimated 20 percent of HNO<sub>3</sub> plants in the United States are equipped with NSCR (Choe et al. 1993). Hence, the emission factor is equal to  $(9.5 \times 0.80) + (2 \times 0.20) = 8$  kg N<sub>2</sub>O per metric ton HNO<sub>3</sub>.

Nitric acid production data for 1990 (see Table 4-58) was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2001). Nitric acid production data for 1991 through 1992 (see Table 4-58) were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2002). Nitric acid production data for 1993 was obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2004). Nitric acid production data for 1994 through 2004 were obtained from *Chemical and Engineering News*, “Facts and Figures” (C&EN 2005). The emission factor range was taken from Choe et al. (1993).

**Table 4-58: Nitric Acid Production (Gg)**

Year	Gg
1990	7,196
1991	7,191
1992	7,379
1993	7,486
1994	7,904
1995	8,018
1996	8,349
1997	8,556
1998	8,421
1999	8,113
2000	7,898
2001	6,416
2002	6,939
2003	6,747
2004	6,703

**Table 4-59: Sources of Uncertainty in N<sub>2</sub>O Emissions from Nitric Acid Production**

Variable	Value	Distribution Type	Uncertainty Range <sup>a</sup>		Reference
			Lower Bound	Upper Bound	
National Production (Gg)	6,703	Normal	-10%	+10%	Expert Judgment
Plants With NSCR (%)	20%	Normal	-10%	+10%	Expert Judgment
Plants Without NSCR (%)	80%	Normal	-10%	+10%	Expert Judgment
Emission Factor for Plants With NSCR (kg N <sub>2</sub> O/tonne HNO <sub>3</sub> )	2.0	Normal	-10%	+10%	IPCC Good Practice
Emission Factor for Plants Without NSCR (kg N <sub>2</sub> O/tonne HNO <sub>3</sub> )	9.5	Normal	-10%	+10%	IPCC Good Practice

<sup>a</sup> Parameters presented represent upper and lower bounds as a percentage of the mean, based on a 95 percent confidence interval.

**Table 4-60: Tier 2 Quantitative Uncertainty Estimates for N<sub>2</sub>O Emissions From Nitric Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Nitric Acid Production	N <sub>2</sub> O	16.6	13.9	19.5	-16%	+17%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## Uncertainty

The overall uncertainty associated with the 2004 N<sub>2</sub>O emissions estimate from nitric acid production was calculated using the IPCC *Good Practice Guidance* Tier 2 methodology. Uncertainty associated with the parameters used to estimate N<sub>2</sub>O emissions included that of production data, the share of U.S. nitric acid production attributable to each emission abatement technology, and the emission factors applied to each abatement technology type. The activity data inputs and their associated uncertainties and distributions are summarized in Table 4-59.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-60. N<sub>2</sub>O emissions from nitric acid production were estimated to be between 13.9 and 19.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 16 percent below to 17 percent above the 2004 emissions estimate of 16.6 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

The nitric acid production value for 2003 has been updated relative to the previous Inventory based on revised production data presented in C&EN (2005). The updated

production data for 2003 resulted in an increase of 0.9 Tg CO<sub>2</sub> Eq. (6 percent) in N<sub>2</sub>O emissions from nitric acid production for that year relative to the previous Inventory.

## Planned Improvements

Planned improvements are focused on assessing the plant-by-plant implementation of NO<sub>x</sub> abatement technologies to more accurately match plant production capacities to appropriate emission factors, instead of using a national profiling of abatement implementation.

## 4.16. Adipic Acid Production (IPCC Source Category 2B3)

Adipic acid production is an anthropogenic source of N<sub>2</sub>O emissions. Worldwide, few adipic acid plants exist. The United States is the major producer, with three companies in four locations accounting for approximately one-third of world production (CW 2005). Adipic acid is a white crystalline solid used in the manufacture of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants. Commercially, it is the most important of the aliphatic dicarboxylic acids, which are used to manufacture polyesters. Approximately 90 percent of all adipic acid



produced in the United States is used in the production of nylon 6,6 (CMR 2001). Food grade adipic acid is also used to provide some foods with a “tangy” flavor (Thiemens and Trogler 1991).

Adipic acid is produced through a two-stage process during which N<sub>2</sub>O is generated in the second stage. The first stage of manufacturing usually involves the oxidation of cyclohexane to form a cyclohexanone/cyclohexanol mixture. The second stage involves oxidizing this mixture with nitric acid to produce adipic acid. N<sub>2</sub>O is generated as a by-product of the nitric acid oxidation stage and is emitted in the waste gas stream (Thiemens and Trogler 1991). Process emissions from the production of adipic acid vary with the types of technologies and level of emission controls employed by a facility. In 1990, two of the three major adipic acid-producing plants had N<sub>2</sub>O abatement technologies in place and, as of 1998, the three major adipic acid production facilities had control systems in place.<sup>14</sup> Only one small plant, representing approximately two percent of production, does not control for N<sub>2</sub>O (Reimer 1999).

N<sub>2</sub>O emissions from this adipic acid production were estimated to be 5.7 Tg CO<sub>2</sub> Eq. (19 Gg) in 2004 (see Table 4-61).

National adipic acid production has increased by approximately 36 percent over the period of 1990 through 2004, to approximately one million metric tons. At the same time, emissions have been significantly reduced due to the widespread installation of pollution control measures.

## Methodology

For two production plants, 1990 to 2002 emission estimates were obtained directly from the plant engineer and account for reductions due to control systems in place at these plants during the time series (Childs 2002, 2003). These estimates were based on continuous emissions monitoring equipment installed at the two facilities. Reported estimates for 2003 and 2004 were unavailable and, thus, were calculated by applying a 4.4 and 4.2 percent production growth rate, respectively. The production for 2003 was obtained through linear interpolation between 2004 and 2002 reported production data. Subsequently, the growth rate for 2004 was based on the change between the estimated

**Table 4-61: N<sub>2</sub>O Emissions from Adipic Acid Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	15.2	49
1998	6.0	19
1999	5.5	18
2000	6.0	19
2001	4.9	16
2002	5.9	19
2003	6.2	20
2004	5.7	19

2003 production data and the reported 2004 production data (see discussion below on sources of production data). For the other two plants, N<sub>2</sub>O emissions were calculated by multiplying adipic acid production by an emission factor (i.e., N<sub>2</sub>O emitted per unit of adipic acid produced) and adjusting for the percentage of N<sub>2</sub>O released as a result of plant-specific emission controls. On the basis of experiments, the overall reaction stoichiometry for N<sub>2</sub>O production in the preparation of adipic acid was estimated at approximately 0.3 metric tons of N<sub>2</sub>O per metric tons of product (Thiemens and Trogler 1991). Emissions are estimated using the following equation:

$$\text{N}_2\text{O emissions} = (\text{production of adipic acid [metric tons \{MT\} of adipic acid]} \times (0.3 \text{ MT N}_2\text{O} / \text{MT adipic acid}) \times (1 - [\text{N}_2\text{O destruction factor} \times \text{abatement system utility factor}]))$$

The “N<sub>2</sub>O destruction factor” represents the percentage of N<sub>2</sub>O emissions that are destroyed by the installed abatement technology. The “abatement system utility factor” represents the percentage of time that the abatement equipment operates during the annual production period. Overall, in the United States, two of the plants employ catalytic destruction, one plant employs thermal destruction, and the smallest plant uses no N<sub>2</sub>O abatement equipment. The N<sub>2</sub>O abatement system destruction factor is assumed to be 95 percent for catalytic abatement and 98 percent for thermal abatement (Reimer et al. 1999, Reimer 1999). For the one plant that uses thermal destruction and for which no reported plant-specific emissions are available, the abatement system utility factor is assumed to be 98 percent.

<sup>14</sup> During 1997, the N<sub>2</sub>O emission controls installed by the third plant operated for approximately a quarter of the year.

For 1990 to 2003, plant-specific production data needed to be estimated where direct emissions measurements were not available. In order to calculate plant-specific production for the two plants, national adipic acid production was allocated to the plant level using the ratio of their known plant capacities to total national capacity for all U.S. plants. The estimated plant production for the two plants was then used for calculating emissions as described above. For 2004, actual plant production data were obtained for these two plants and used for emissions calculations.

National adipic acid production data (see Table 4-62) for 1990 through 2002 were obtained from the American Chemistry Council (ACC 2003). Production Data for 2003 were estimated based on linear interpolation of 2002 and 2004 reported data. Production data for 2004 were obtained from *Chemical Week*, Product Focus: Adipic Acid (CW 2005). Plant capacity data for 1990 through 1994 were obtained from *Chemical and Engineering News*, “Facts and Figures” and “Production of Top 50 Chemicals” (C&EN 1992, 1993, 1994, 1995). Plant capacity data for 1995 and 1996 were kept the same as 1994 data. The 1997 plant capacity data were taken from *Chemical Market Reporter* “Chemical Profile: Adipic Acid” (CMR 1998). The 1998 plant capacity data for all four plants and 1999 plant capacity data for three of the plants were obtained from *Chemical Week*, Product Focus: Adipic Acid/Adiponitrile (CW 1999). Plant capacity data for 2000 for three of the plants were updated using *Chemical Market Reporter*, “Chemical Profile: Adipic Acid” (CMR

2001). For 2001 through 2004, the plant capacities for these three plants were kept the same as the year 2000 capacities. Plant capacity data for 1999 to 2004 for the one remaining plant was kept the same as 1998.

## Uncertainty

The overall uncertainty associated with the 2004 N<sub>2</sub>O emissions estimate from adipic acid production was calculated using the IPCC *Good Practice Guidance* Tier 2 methodology. Uncertainty associated with the parameters used to estimate N<sub>2</sub>O emissions included that of company specific production data, industry wide estimated production growth rates, emission factors for abated and unabated emissions, and company specific historical emissions estimates. The activity data inputs and their associated uncertainties and distributions are summarized in Table 4-63.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-64. N<sub>2</sub>O emissions from adipic acid production were estimated to be between 3.2 and 8.3 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 45 percent below to 44 percent above the 2004 emission estimate of 5.7 Tg CO<sub>2</sub> Eq.

## Recalculations Discussion

The adipic acid industry-wide production value for 2003 was updated through linear interpolation between 2002 and 2004 reported production data. Newly published adipic acid production figures for 2004 were obtained from *Chemical Week* (CW 2005). The updated production data for 2003 resulted in an increase of 0.2 Tg CO<sub>2</sub> Eq. (3 percent) in N<sub>2</sub>O emissions from adipic acid production for that year relative to the previous Inventory.

## Planned Improvements

Improvement efforts will be focused on obtaining direct measurement data from the remaining two plants when and if they become available. If they become available, cross verification with top-down approaches will provide a useful Tier 2 level QC check. Also, additional information on the actual performance of the latest catalytic and thermal abatement equipment at plants with continuous emission monitoring may support the re-evaluation of current default abatement values.

**Table 4-62: Adipic Acid Production (Gg)**

Year	Gg
1990	735
1991	708
1992	724
1993	769
1994	821
1995	830
1996	839
1997	871
1998	862
1999	907
2000	925
2001	835
2002	921
2003	961
2004	1,002

**Table 4-63: Sources of Uncertainty in N<sub>2</sub>O Emissions from Adipic Acid Production**

Variable	Value	Distribution Type	Uncertainty Range <sup>a</sup>		Reference
			Lower Bound	Upper Bound	
Company Specific Production (Gg): Plant 1	17	Normal	-10%	+10%	Expert Judgment
Company Specific Production (Gg): Plant 4	400	Normal	-10%	+10%	Expert Judgment
Estimated Production Growth Rates (2002-2003) (%): Plants 2 and 3	4%	Normal	-25%	+25%	Expert Judgment
Estimated Production Growth Rates (2003-2004) (%): Plants 2 and 3	4%	Normal	-25%	+25%	Expert Judgment
N <sub>2</sub> O Destruction Factor (%): Plant 4	98%	Normal	-5%	+5%	IPCC Good Practice
Abatement System Utility Factor (%): Plant 4	98%	Normal	-5%	+5%	Expert Judgment
2002 Emission Estimate (Tg CO <sub>2</sub> Eq.): Plant 2	Confidential	Normal	-5%	+5%	Expert Judgment
2002 Emission Estimate (Tg CO <sub>2</sub> Eq.): Plant 3	Confidential	Normal	-5%	+5%	Expert Judgment

<sup>a</sup> Parameters presented represent upper and lower bounds as a percentage of the mean, based on a 95 percent confidence interval.

**Table 4-64: Tier 2 Quantitative Uncertainty Estimates for N<sub>2</sub>O Emissions from Adipic Acid Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup> (Tg CO <sub>2</sub> Eq.)			
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Adipic Acid Production	N <sub>2</sub> O	5.7	3.2	8.3	-45%	+44%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

## 4.17. Substitution of Ozone Depleting Substances (IPCC Source Category 2F)

Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are used as alternatives to several classes of ozone-depleting substances (ODSs) that are being phased out under the terms of the *Montreal Protocol* and the Clean Air Act Amendments of 1990.<sup>15</sup> Ozone depleting substances—chlorofluorocarbons (CFCs), halons, carbon tetrachloride, methyl chloroform, and hydrochlorofluorocarbons (HCFCs)—are used in a variety of industrial applications including refrigeration and air conditioning equipment, solvent cleaning, foam production,

sterilization, fire extinguishing, and aerosols. Although HFCs and PFCs, are not harmful to the stratospheric ozone layer, they are potent greenhouse gases. Emission estimates for HFCs and PFCs used as substitutes for ODSs are provided in Table 4-65 and Table 4-66.

In 1990 and 1991, the only significant emissions of HFCs and PFCs as substitutes to ODSs were relatively small amounts of HFC-152a—a component of the refrigerant blend R-500 used in chillers—and HFC-134a in refrigeration end-uses. Beginning in 1992, HFC-134a was used in growing amounts as a refrigerant in motor vehicle air-conditioners and in refrigerant blends such as R-404A.<sup>16</sup> In 1993, the use of HFCs in foam production and as an aerosol propellant began, and in 1994 these compounds also found applications

<sup>15</sup> [42 U.S.C § 7671, CAA § 601]

<sup>16</sup> R-404A contains HFC-125, HFC-143a, and HFC-134a.

**Table 4-65: Emissions of HFCs and PFCs from ODS Substitutes (Tg CO<sub>2</sub> Eq.)**

Gas	1990	1998	1999	2000	2001	2002	2003	2004
HFC-23	+	+	0.1	0.1	0.1	0.1	0.1	0.1
HFC-32	+	0.3	0.3	0.3	0.3	0.3	0.4	0.4
HFC-125	+	8.8	10.0	11.2	12.3	13.4	14.7	16.3
HFC-134a	+	35.2	40.2	45.4	49.7	53.5	56.8	61.6
HFC-143a	+	5.2	6.6	8.2	10.1	12.2	14.6	17.3
HFC-236fa	+	0.4	0.9	1.4	1.8	2.1	2.3	2.3
CF <sub>4</sub>	+	+	+	+	+	+	+	+
Others*	0.4	4.6	4.8	4.6	4.5	4.6	4.6	5.3
<b>Total</b>	<b>0.4</b>	<b>54.5</b>	<b>62.8</b>	<b>71.2</b>	<b>78.6</b>	<b>86.2</b>	<b>93.5</b>	<b>103.3</b>

+ Does not exceed 0.05 Tg CO<sub>2</sub> Eq.

\* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee, and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications. For estimating purposes, the GWP value used for PFC/PFPEs was based upon C<sub>6</sub>F<sub>14</sub>.

Note: Totals may not sum due to independent rounding.

**Table 4-66: Emissions of HFCs and PFCs from ODS Substitution (Mg)**

Gas	1990	1998	1999	2000	2001	2002	2003	2004
HFC-23	+	4	4	5	5	6	6	7
HFC-32	+	430	439	443	463	501	557	631
HFC-125	+	3,134	3,571	4,006	4,390	4,787	5,262	5,821
HFC-134a	+	27,058	30,902	34,927	38,196	41,170	43,664	47,391
HFC-143a	+	1,369	1,738	2,162	2,647	3,203	3,834	4,543
HFC-236fa	+	64	142	214	281	341	369	367
CF <sub>4</sub>	+	1	1	1	1	2	2	3
Others*	M	M	M	M	M	M	M	M

M (Mixture of Gases)

+ Does not exceed 0.5 Mg

\* Others include HFC-152a, HFC-227ea, HFC-245fa, HFC-4310mee and PFC/PFPEs, the latter being a proxy for a diverse collection of PFCs and perfluoropolyethers (PFPEs) employed for solvent applications.

as solvents and sterilants. In 1995, ODS substitutes for halons entered widespread use in the United States as halon production was phased-out.

The use and subsequent emissions of HFCs and PFCs as ODS substitutes has been increasing from small amounts in 1990 to 103.3 Tg CO<sub>2</sub> Eq. in 2004. This increase was in large part the result of efforts to phase out CFCs and other ODSs in the United States. In the short term, this trend is expected to continue, and will likely accelerate over the next decade as HCFCs, which are interim substitutes in many applications, are themselves phased-out under the provisions of the Copenhagen Amendments to the *Montreal Protocol*. Improvements in the technologies associated with the use of these gases and the introduction of alternative gases and technologies, however, may help to offset this anticipated increase in emissions.

The end-use sectors that contribute the most toward emissions of HFCs and PFCs as ODS substitutes include

refrigeration and air-conditioning (88.4 Tg CO<sub>2</sub> Eq., or approximately 85 percent), aerosols (11.1 Tg CO<sub>2</sub> Eq., or approximately 11 percent), and solvents (1.6 Tg CO<sub>2</sub> Eq., or approximately 2 percent). Within the refrigeration and air-conditioning end-use sector, motor vehicle air-conditioning was the highest emitting end-use (31.9 Tg CO<sub>2</sub> Eq.), followed by retail food and refrigerated transport. In the aerosols end-use sector, non-metered-dose inhaler (MDI) emissions make up a majority of the end-use sector emissions.

## Methodology

A detailed Vintaging Model of ODS-containing equipment and products was used to estimate the actual—versus potential—emissions of various ODS substitutes, including HFCs and PFCs. The name of the model refers to the fact that the model tracks the use and emissions of various compounds for the annual “vintages” of new equipment that enter service in each end-use. This

Vintaging Model predicts ODS and ODS substitute use in the United States based on modeled estimates of the quantity of equipment or products sold each year containing these chemicals and the amount of the chemical required to manufacture and/or maintain equipment and products over time. Emissions for each end-use were estimated by applying annual leak rates and release profiles, which account for the lag in emissions from equipment as they leak over time. By aggregating the data for more than 50 different end-uses, the model produces estimates of annual use and emissions of each compound. Further information on the Vintaging Model is contained in Annex 3.8.

## Uncertainty

Given that emissions of ODS substitutes occur from thousands of different kinds of equipment and from millions of point and mobile sources throughout the United States, emission estimates must be made using analytical tools such as the Vintaging Model or the methods outlined in IPCC/UNEP/OECD/IEA (1997). Though the model is more comprehensive than the IPCC default methodology, significant uncertainties still exist with regard to the levels of equipment sales, equipment characteristics, and end-use emissions profiles that were used to estimate annual emissions for the various compounds.

The Vintaging Model estimates emissions from over 50 end-uses. The uncertainty analysis, however, quantifies the level of uncertainty associated with the aggregate emissions resulting from the top 15 end-uses and 5 others. These end-uses together account for 95 percent of emissions from this source category. In an effort to improve the uncertainty analysis, additional end-uses are added annually, with the intention that over time uncertainty for all emissions from the Vintaging Model will be fully characterized. This year, an additional 5 end-uses were included in the uncertainty

estimate. Since the foams sector is not represented in the top 15, the two highest emitting foams end-uses were chosen to represent this sector, and two MDI aerosols end-uses were included to represent the MDI portion of the aerosols sector. Any end-uses included in previous years' uncertainty analysis were included in the current uncertainty analysis, whether or not those end-uses were included in the top 95 percent of emissions from ODS Substitutes.

In order to calculate uncertainty, functional forms were developed to simplify some of the complex "vintaging" aspects of some end-use sectors, especially with respect to refrigeration and air-conditioning, and to a lesser degree, fire extinguishing. These sectors calculate emissions based on the entire lifetime of equipment, not just equipment put into commission in the current year, thereby necessitating simplifying equations. The functional forms used variables that included growth rates, emission factors, transition from ODSs, change in charge size as a result of the transition, disposal quantities, disposal emission rates, and either stock for the current year or original ODS consumption. Uncertainty was estimated around each variable within the functional forms based on expert judgment, and a Monte Carlo analysis was performed. The most significant sources of uncertainty for this source category include the emission factors for mobile air-conditioning and retail food refrigeration, as well as the stock (MT) of retail food refrigerant.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-67. Substitution of ozone depleting substances HFC and PFC emissions were estimated to be between 90.5 and 124.4 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 13 percent below to 20 percent above the emission estimate of 103.3 Tg CO<sub>2</sub> Eq.

**Table 4-67: Tier 2 Quantitative Uncertainty Estimates for HFC and PFC Emissions from ODS Substitutes (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gases	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Substitution of Ozone Depleting Substances	HFCs and PFCs	103.3	90.5	124.4	-13%	+20%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



## Recalculations Discussion

An extensive review of the chemical substitution trends, market sizes, growth rates, and charge sizes, together with input from industry representatives, resulted in updated assumptions for the Vintaging Model. These changes resulted in an average annual net decrease of 2.0 Tg CO<sub>2</sub> Eq. (3 percent) in HFC and PFC emissions from the substitution of ozone depleting substances for the period 1990 through 2003.

### 4.18. HCFC-22 Production (IPCC Source Category 2E1)

Trifluoromethane (HFC-23 or CHF<sub>3</sub>) is generated as a by-product during the manufacture of chlorodifluoromethane (HCFC-22), which is primarily employed in refrigeration and air conditioning systems and as a chemical feedstock for manufacturing synthetic polymers. Between 1990 and 2000, U.S. production of HCFC-22 increased significantly as HCFC-22 replaced chlorofluorocarbons (CFCs) in many applications. Since 2000, however, U.S. production has declined to levels near those of the early to mid 1990s. Because HCFC-22 depletes stratospheric ozone, its production for non-feedstock uses is scheduled to be phased out by 2020 under the U.S. Clean Air Act.<sup>17</sup> Feedstock production, however, is permitted to continue indefinitely.

HCFC-22 is produced by the reaction of chloroform (CHCl<sub>3</sub>) and hydrogen fluoride (HF) in the presence of a

catalyst, SbCl<sub>5</sub>. The reaction of the catalyst and HF produces SbCl<sub>x</sub>F<sub>y</sub>, (where x + y = 5), which reacts with chlorinated hydrocarbons to replace chlorine atoms with fluorine. The HF and chloroform are introduced by submerged piping into a continuous-flow reactor that contains the catalyst in a hydrocarbon mixture of chloroform and partially fluorinated intermediates. The vapors leaving the reactor contain HCFC-21 (CHCl<sub>2</sub>F), HCFC-22 (CHClF<sub>2</sub>), HFC-23 (CHF<sub>3</sub>), HCl, chloroform, and HF. The under-fluorinated intermediates (HCFC-21) and chloroform are then condensed and returned to the reactor, along with residual catalyst, to undergo further fluorination. The final vapors leaving the condenser are primarily HCFC-22, HFC-23, HCl and residual HF. The HCl is recovered as a useful byproduct, and the HF is removed. Once separated from HCFC-22, the HFC-23 is generally vented to the atmosphere as an unwanted by-product, but it is sometimes captured for use in a limited number of applications.

Emissions of HFC-23 in 2004 were estimated to be 15.6 Tg CO<sub>2</sub> Eq. (1.3 Gg) (Table 4-68). This quantity represents a 26 percent increase from 2003 emissions and a 55 percent decline from 1990 emissions. The increase from 2003 emissions is due to an increase in HCFC-22 production, while the decline from 1990 emissions is primarily due to the steady decline in the emission rate of HFC-23 (i.e., the amount of HFC-23 emitted per kilogram of HCFC-22 manufactured).

**Table 4-68: HFC-23 Emissions from HCFC-22 Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	35.0	3
1998	40.1	3
1999	30.4	3
2000	29.8	3
2001	19.8	2
2002	19.8	2
2003	12.3	1
2004	15.6	1

**Table 4-69: HCFC-22 Production (Gg)**

Year	Gg
1990	139
1991	143
1992	150
1993	132
1994	147
1995	155
1996	166
1997	165
1998	183
1999	166
2000	187
2001	152
2002	144
2003	138
2004	155

<sup>17</sup> As construed, interpreted, and applied in the terms and conditions of the *Montreal Protocol on Substances that Deplete the Ozone Layer*. [42 U.S.C. §7671m(b), CAA §614]

**Table 4-70: Tier 1 Quantitative Uncertainty Estimates for HFC-23 Emissions from HCFC-22 Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
HCFC-22 Production	HFC-23	15.6	14.0	17.2	-10%	+10%

<sup>a</sup> Range of emission reflect a 95 percent confidence interval.

Three HCFC-22 production plants operated in the United States in 2004, two of which used thermal oxidation to significantly lower their HFC-23 emissions.

## Methodology

The methodology employed for estimating emissions is based upon measurements at individual HCFC-22 production plants. Plants using thermal oxidation to abate their HFC-23 emissions monitor the performance of their oxidizers to verify that the HFC-23 is almost completely destroyed. The other plants periodically measure HFC-23 concentrations in the output stream using gas chromatography. This information is combined with information on quantities of critical feed components (e.g., HF) and/or products (HCFC-22) to estimate HFC-23 emissions using a material balance approach. HFC-23 concentrations are determined at the point the gas leaves the chemical reactor; therefore, estimates also include fugitive emissions.

Production data and emission estimates were prepared in cooperation with the U.S. manufacturers of HCFC-22 (ARAP 1997, 1999, 2000, 2001, 2002, 2003, 2004; 2005; RTI 1997). Annual estimates of U.S. HCFC-22 production are presented in Table 4-69.

## Uncertainty

A high level of confidence has been attributed to the HFC-23 concentration data employed because measurements were conducted frequently and accounted for day-to-day and process variability. The results of the Tier 1 quantitative uncertainty analysis are summarized in Table 4-70. HFC-23 emissions from HCFC-22 production were estimated to be between 14.0 and 17.2 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of 10 percent above and 10 percent below the 2004 emission estimate of 15.6 Tg CO<sub>2</sub> Eq.

## 4.19. Electrical Transmission and Distribution (IPCC Source Category 2F7)

The largest use of SF<sub>6</sub>, both in the United States and internationally, is as an electrical insulator and interrupter in equipment that transmits and distributes electricity (RAND 2004). The gas has been employed by the electric power industry in the United States since the 1950s because of its dielectric strength and arc-quenching characteristics. It is used in gas-insulated substations, circuit breakers, and other switchgear. Sulfur hexafluoride has replaced flammable insulating oils in many applications and allows for more compact substations in dense urban areas.

Fugitive emissions of SF<sub>6</sub> can escape from gas-insulated substations and switch gear through seals, especially from older equipment. The gas can also be released during equipment manufacturing, installation, servicing, and disposal. Emissions of SF<sub>6</sub> from electrical transmission and distribution systems were estimated to be 13.8 Tg CO<sub>2</sub> Eq. (0.6 Gg) in 2004. This quantity represents a 52 percent decrease from the estimate for 1990 (see Table 4-71 and

**Table 4-71: SF<sub>6</sub> Emissions from Electric Power Systems and Original Equipment Manufacturers (Tg CO<sub>2</sub> Eq.)**

Year	Electric Power Systems	Original Equipment Manufacturers	
		Manufacturers	Total
1990	28.3	0.3	28.6
1998	16.4	0.4	16.7
1999	15.5	0.6	16.1
2000	14.6	0.7	15.3
2001	14.7	0.7	15.3
2002	13.8	0.7	14.5
2003	13.4	0.7	14.0
2004	13.1	0.7	13.8

**Table 4-72: SF<sub>6</sub> Emissions from Electric Power Systems and Original Equipment Manufactures (Gg)**

Year	Emissions
1990	1.2
1998	0.7
1999	0.7
2000	0.6
2001	0.6
2002	0.6
2003	0.6
2004	0.6

Table 4-72). This decrease is believed to be a response to increases in the price of SF<sub>6</sub> during the 1990s and to growing awareness of the environmental impact of SF<sub>6</sub> emissions, through programs such as the EPA's SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems.

## Methodology

The estimates of emissions from electric transmission and distribution are comprised of emissions from electric power systems and emissions from the manufacture of electrical equipment. The methodologies for estimating both sets of emissions are described below.

### 1999 to 2004 Emissions from Electric Power Systems

Emissions from electric power systems from 1999 to 2004 were estimated based on: (1) reporting from utilities participating in EPA's SF<sub>6</sub> Emissions Reduction Partnership for Electric Power Systems, which began in 1999; and, (2) utilities' transmission miles as reported in the 2001 and 2004 Utility Data Institute (UDI) Directories of Electric Power Producers and Distributors (UDI 2001, 2004). (Transmission miles are defined as the miles of lines carrying voltages above 34.5 kV.) Over the period from 1999 to 2004, participating utilities represented between 31 percent and 39 percent of total U.S. transmission miles. For each year, the emissions reported by participating utilities were added to the emissions estimated for utilities that do not participate in the EPA's SF<sub>6</sub> Emission Reduction Partnership (i.e., non-partners).

Emissions from utilities participating in EPA's SF<sub>6</sub> Emission Reduction Partnership were estimated using a combination of reported data and, where reported data were unavailable, interpolated or extrapolated data. If a partner utility did not provide data for a historical year,

emissions were interpolated between years for which data were available. For 2004, if no data was provided, estimates were calculated based on historical trends or partner-specific emission reduction targets (i.e., it was assumed that emissions would decline linearly towards a partners' future stated goal). In 2004, non-reporting partners account for approximately 2 percent of the total emissions attributable to utilities involved in the SF<sub>6</sub> Emission Reduction Partnership.

Emissions from non-partners in every year since 1999 were estimated using the results of a regression analysis that showed that the emissions of reporting utilities were most strongly correlated with their transmission miles. The results of this analysis are not surprising given that, in the United States, SF<sub>6</sub> is contained primarily in transmission equipment rated at or above 34.5 kV. The equations were developed based on the 1999 SF<sub>6</sub> emissions reported by 49 partner utilities (representing approximately 31 percent of U.S. transmission miles), and 2000 transmission mileage data obtained from the 2001 UDI Directory of Electric Power Producers and Distributors (UDI 2001). Two equations were developed, one for small and one for large utilities (i.e., with less or more than 10,000 transmission miles, respectively). The distinction between utility sizes was made because the regression analysis showed that the relationship between emissions and transmission miles differed for small and large transmission networks. The same equations were used to estimate non-partner emissions in 1999 and every year thereafter because it was assumed that non-partners have not implemented any changes that have resulted in reduced emissions since 1999.

The regression equations are:

**Non-partner small utilities (less than 10,000 transmission miles, in kilograms):**

$$\text{Emissions} = 0.874 \times \text{Transmission Miles}$$

**Non-partner large utilities (more than 10,000 transmission miles, in kilograms):**

$$\text{Emissions} = 0.558 \times \text{Transmission Miles}$$

Data on transmission miles for each non-partner utility for the years 2000 and 2003 was obtained from the 2001 and 2004 UDI Directories of Electric Power Producers and Distributors, respectively (UDI 2001, 2004). Given that the U.S. transmission system grew by over 14,000 miles between 2000 and 2003, and that this increase probably occurred

gradually, transmission mileage was assumed to increase exponentially at an annual rate of 0.7 percent between 2000 and 2003. This growth rate is assumed to continue through 2004.

As a final step, total emissions were determined for each year by summing the partner emissions (reported to the EPA's SF<sub>6</sub> Emission Reduction Partnership for Electric Power Systems), and the non-partner emissions (determined using the 1999 regression equation).

### 1990 to 1998 Emissions from Electric Power Systems

Because most participating utilities reported emissions only for 1999 through 2004, modeling SF<sub>6</sub> emissions from electric power systems for the years 1990 through 1998 was necessary. To do so, it was assumed that during this period, U.S. emissions followed the same trajectory as global emissions from this source. To estimate global emissions, the RAND survey of global SF<sub>6</sub> sales to electric utilities was used, together with the following equation, which is derived from the equation for emissions in the IPCC *Good Practice Guidance* (IPCC 2000):

$$\text{Emissions (kilograms)} = \text{SF}_6 \text{ purchased to refill existing equipment (kilograms)} + \text{nameplate capacity of retiring equipment (kilograms)}$$

Note that the above equation holds whether the gas from retiring equipment is released or recaptured; if the gas is recaptured, it is used to refill existing equipment, lowering the amount of SF<sub>6</sub> purchased by utilities for this purpose.

Sulfur hexafluoride purchased to refill existing equipment in a given year was assumed to be approximately equal to the SF<sub>6</sub> purchased by utilities in that year. Gas purchases by utilities and equipment manufacturers from 1961 through 2001 are available from the RAND (2004) survey. To estimate the quantity of SF<sub>6</sub> released or recovered from retiring equipment, the nameplate capacity of retiring equipment in a given year was assumed to equal 77.5 percent of the amount of gas purchased by electrical equipment manufacturers 30 years previous (e.g., in 1990, the nameplate capacity of retiring equipment was assumed to equal 77.5 percent of the gas purchased in 1960). The remaining 22.5 percent was assumed to have been emitted at the time of manufacture. The 22.5 percent emission rate is an average of IPCC SF<sub>6</sub> emission rates for Europe and Japan for years before 1996 (IPCC 2000). The 30-year lifetime for electrical equipment is also drawn from IPCC (2000). The results

of the two components of the above equation were then summed to yield estimates of global SF<sub>6</sub> emissions from 1990 through 1998.

To estimate U.S. emissions for 1990 through 1998, estimated global emissions for each year from 1990 through 1998 were divided by the estimated global emissions from 1999. The result was a time series of factors that express each year's global emissions as a multiple of 1999 global emissions. To estimate historical U.S. emissions, the factor for each year was multiplied by the estimated U.S. emissions of SF<sub>6</sub> from electric power systems in 1999 (estimated to be 15.5 Tg CO<sub>2</sub> Eq.).

### 1990 to 2004 Emissions from Manufacture of Electrical Equipment

The 1990 to 2004 emissions estimates for original equipment manufacturers (OEMs) were derived by assuming that manufacturing emissions equal 10 percent of the quantity of SF<sub>6</sub> charged into new equipment. The quantity of SF<sub>6</sub> charged into new equipment was estimated based on statistics compiled by the National Electrical Manufacturers Association (NEMA). These statistics were provided for 1990 to 2000; the quantities of SF<sub>6</sub> charged into new equipment for 2001 to 2004 were assumed to equal that charged into equipment in 2000. The 10 percent emission rate is the average of the "ideal" and "realistic" manufacturing emission rates (4 percent and 17 percent, respectively) identified in a paper prepared under the auspices of the International Council on Large Electric Systems (CIGRE) in February 2002 (O'Connell et al. 2002).

## Uncertainty

To estimate the uncertainty associated with emissions of SF<sub>6</sub> from electric transmission and distribution, EPA estimated the uncertainties associated with three variables: (1) emissions from electric power systems that participate in EPA's SF<sub>6</sub> Emission Reduction Partnership, (2) emissions from electric power systems that do not participate in the Partnership, and (3) emissions from manufacturers of electrical equipment. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emissions estimate.

The cumulative uncertainty of all partner data was estimated to be 5 percent, based on error propagation. There are two sources of uncertainty associated with the regression

**Table 4-73: Tier 2 Quantitative Uncertainty Estimates for SF<sub>6</sub> Emissions from Electrical Transmission and Distribution (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Electrical Transmission and Distribution	SF <sub>6</sub>	13.8	12.0	15.7	-13%	+13%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

equations used to estimate emissions in 2004 from non-partners: (1) uncertainty in the coefficients (as defined by the regression standard error estimate); and, (2) the uncertainty in total transmission miles for non-partners, which is assumed to be 10 percent. In addition, there is uncertainty associated with the assumption that the emission factor used for non-partner utilities (which accounted for approximately 65 percent of U.S. transmission miles) will remain at levels defined by partners who reported in 1999. However, the last source of uncertainty was not modeled.

For OEMs, uncertainty estimates are based on the assumption that SF<sub>6</sub> statistics obtained from NEMA have an uncertainty of 20 percent. Additionally, the OEMs SF<sub>6</sub> emissions rate has an uncertainty bounded by the proposed “actual” and “ideal” emission rates defined in O’Connell, et al. (2002). That is, the uncertainty in the emission rate is approximately 65 percent.

A Monte Carlo analysis was applied to estimate the overall uncertainty of the 2004 emission estimate for SF<sub>6</sub> from electrical transmission and distribution. For each defined parameter (i.e., equation coefficient, transmission mileage, and partner-reported and partner-estimated SF<sub>6</sub> emissions data for electric power systems; and SF<sub>6</sub> emission rate and statistics for OEMs), random variables were selected from probability density functions, all assumed to have normal distributions about the mean. The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-73. Electrical Transmission and Distribution SF<sub>6</sub> emissions were estimated to be between 12.0 and 15.7 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 13 percent below and 13 percent above the emission estimate of 13.8 Tg CO<sub>2</sub> Eq.

In addition to the uncertainty quantified above, there is uncertainty associated with using global SF<sub>6</sub> sales data

to estimate U.S. emission trends from 1990 through 1999. However, the trend in global emissions implied by sales of SF<sub>6</sub> appears to reflect the trend in global emissions implied by changing SF<sub>6</sub> concentrations in the atmosphere. That is, emissions based on global sales declined by 21 percent between 1995 and 1998, and emissions based on atmospheric measurements declined by 27 percent over the same period. However, U.S. emission patterns may differ from global emission patterns.

## 4.20. Semiconductor Manufacture (IPCC Source Category 2F6)

The semiconductor industry uses multiple long-lived fluorinated gases in plasma etching and plasma enhanced chemical vapor deposition (PECVD) processes to produce semiconductor products. The gases most commonly employed are trifluoromethane (HFC-23 or CHF<sub>3</sub>), perfluoromethane (CF<sub>4</sub>), perfluoroethane (C<sub>2</sub>F<sub>6</sub>), nitrogen trifluoride (NF<sub>3</sub>), and sulfur hexafluoride (SF<sub>6</sub>), although other compounds such as perfluoropropane (C<sub>3</sub>F<sub>8</sub>) and perfluorocyclobutane (c-C<sub>4</sub>F<sub>8</sub>) are also used. The exact combination of compounds is specific to the process employed.

A single 300 mm silicon wafer that yields between 400 to 500 semiconductor products (devices or chips) may require as many as 100 distinct fluorinated-gas-using process steps, principally to deposit and pattern dielectric films. Plasma etching (or patterning) of dielectric films, such as silicon dioxide and silicon nitride, is performed to provide pathways for conducting material to connect individual circuit components in each device. The patterning process uses plasma-generated fluorine atoms, which chemically react with exposed dielectric film, to selectively remove the desired portions of the film. The material removed as well as undissociated fluorinated gases flow into waste



streams and, unless emission abatement systems are employed, into the atmosphere. PECVD chambers, used for depositing dielectric films, are cleaned periodically using fluorinated and other gases. During the cleaning cycle the gas is converted to fluorine atoms in plasma, which etches away residual material from chamber walls, electrodes, and chamber hardware. Undissociated fluorinated gases and other products pass from the chamber to waste streams and, unless abatement systems are employed, into the atmosphere. In addition to emissions of unreacted gases, some fluorinated compounds can also be transformed in the plasma processes into different fluorinated compounds which are then exhausted, unless abated, into the atmosphere. For example, when C<sub>2</sub>F<sub>6</sub> is used in cleaning or etching, CF<sub>4</sub> is generated and emitted as a process by-product. Besides dielectric film etching and PECVD chamber cleaning, much smaller quantities of fluorinated gases are used to etch polysilicon films and refractory metal films like tungsten.

For 2004, total weighted emissions of all fluorinated greenhouse gases by the U.S. semiconductor industry were estimated to be 4.7 Tg CO<sub>2</sub> Eq. Combined emissions of all fluorinated greenhouse gases are presented in Table 4-74 and

Table 4-75, below. The rapid growth of this industry and the increasing complexity of semiconductor products which use more PFCs in the production process have led to an increase in emissions of 61 percent since 1990. The emissions growth rate began to slow after 1997, and emissions declined by 35 percent between 1999 and 2004. The initial implementation of PFC emission reduction methods such as process optimization and abatement technologies is responsible for this decline.

## Methodology

Emissions from semiconductor manufacturing were estimated using three distinct methods, one each for the periods 1990 through 1994, 1995 through 1999, and 2000 and beyond. For 1990 through 1994, emissions were estimated using the most recent version of EPA's PFC Emissions Vintage Model (PEVM) (Burton and Beizaie 2001).<sup>18</sup> PFC emissions per square centimeter of silicon increase as the number of layers in semiconductor devices increases. Thus, PEVM incorporates information on the two attributes of semiconductor devices that affect the number of layers: (1) linewidth technology (the smallest feature size, which leads

**Table 4-74: PFC, HFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Tg CO<sub>2</sub> Eq.)**

Year	1990	1998	1999	2000	2001	2002	2003	2004
CF <sub>4</sub>	0.7	1.8	1.8	1.8	1.3	1.1	1.0	1.2
C <sub>2</sub> F <sub>6</sub>	1.5	3.6	3.7	3.0	2.1	2.2	2.1	2.2
C <sub>3</sub> F <sub>8</sub>	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0
C <sub>4</sub> F <sub>8</sub>	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1
HFC-23	0.2	0.4	0.4	0.3	0.2	0.2	0.2	0.2
SF <sub>6</sub>	0.5	1.3	1.3	1.1	0.8	0.7	0.8	0.9
NF <sub>3</sub> *	0.0	0.1	0.1	0.1	0.1	0.3	0.2	0.3
<b>Total</b>	<b>2.9</b>	<b>7.1</b>	<b>7.2</b>	<b>6.3</b>	<b>4.5</b>	<b>4.4</b>	<b>4.3</b>	<b>4.7</b>

Note: Totals may not sum due to independent rounding.

\* NF<sub>3</sub> emissions are presented for informational purposes, using a GWP of 8,000, and are not included in totals.

**Table 4-75: PFC, HFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Mg)**

Year	1990	1998	1999	2000	2001	2002	2003	2004
CF <sub>4</sub>	115	277	281	281	202	175	161	185
C <sub>2</sub> F <sub>6</sub>	160	391	397	324	231	244	228	245
C <sub>3</sub> F <sub>8</sub>	0	0	0	17	14	9	13	6
C <sub>4</sub> F <sub>8</sub>	0	0	0	0	0	5	8	9
HFC-23	15	37	37	23	16	15	17	20
SF <sub>6</sub>	22	54	55	46	31	28	35	38
NF <sub>3</sub>	3	9	9	11	12	32	30	31

<sup>18</sup> The most recent version of this model is v.3.2.0506.0507, completed in September 2005.

to an increasing number of layers),<sup>19</sup> and (2) product type (memory vs. logic).<sup>20</sup> PEVM derives historical consumption of silicon (i.e., square centimeters) by linewidth technology from published data on annual wafer starts and average wafer size (Burton and Beizaie 2001). For each linewidth technology, a weighted average number of layers is estimated using VLSI product-specific worldwide silicon demand data in conjunction with complexity factors (i.e., the number of layers per integrated circuit) specific to product type (Burton and Beizaie 2001; ITRS 2005). The distribution of memory/logic devices ranges over the period covered from 52 percent logic devices in 1995 to 59 percent logic devices in 2000. These figures were used to determine emission factors that express emissions per average layer per unit of area of silicon consumed during product manufacture. The per-layer emission factor was based on the total annual emissions reported by participants in EPA's PFC Reduction/Climate Partnership for the Semiconductor Industry in 1995 and later years.

For 1995 through 1999, total U.S. emissions were extrapolated from the total annual emissions reported by the Partnership participants (Burton and Mallya 2005). The emissions reported by the participants were divided by the ratio of the total layer-weighted capacity of the plants operated by the participants and the total layer-weighted capacity of all of the semiconductor plants in the United States; this ratio represents the share of layer-weighted capacity attributable to partnership participants. The layer-weighted capacity of a plant (or group of plants) consists of the silicon capacity of that plant multiplied by the estimated number of layers used to fabricate products at that plant. This method assumes that participants and non-participants have similar capacity utilizations and per-layer emission factors. Plant capacity, linewidth technology, products

manufactured information is contained in the World Fab Watch (WFW) database, which is updated quarterly (see for example, Semiconductor Equipment and Materials Industry 2005).

The U.S. estimate for the years 2000 through 2004—the period during which partners began the consequential application of PFC-reduction measures—used a different estimation method. The emissions reported by Partnership participants for each year were accepted as the quantity emitted from the share of the industry represented by those Partners. Remaining emissions (those from non-partners), however, were estimated using PEVM and the method described above. (Non-partners are assumed not to have implemented any PFC-reduction measures, and PEVM models emissions without such measures.) The portion of the U.S. total attributed to non-Partners is obtained by multiplying PEVM's total U.S. figure by the non-partner share of total layer-weighted silicon capacity for each year (as described above). Annual updates to PEVM reflect published figures for actual silicon consumption from VLSI Research, Inc. as well as revisions and additions to the world population of semiconductor manufacturing plants (see Semiconductor Equipment and Materials Industry 2005).<sup>21</sup>

Two different approaches were also used to estimate the distribution of emissions of specific PFCs. Before 1999, when there was no consequential adoption of PFC-reducing measures, a fixed distribution was assumed to apply to the entire U.S. industry. This distribution was based upon the average PFC purchases by semiconductor manufacturers during this period and the application of IPCC default emission factors for each gas (Burton and Beizaie 2001). For the 2000 through 2004 period, the 1990 through 1999 distribution was assumed to apply to the non-Partners. Partners, however, began to report gas-specific emissions

<sup>19</sup> By decreasing features of IC components, more components can be manufactured per device, which increases its functionality. However, as those individual components shrink it requires more layers to interconnect them to achieve the functionality. For example, a microprocessor manufactured with the smallest feature sizes (65 nm) might contain as many as 1 billion transistors and requires as many as 11 layers of component interconnects to achieve functionality while a device manufactured with 130 nm feature size might contain a few hundred million transistors and require 8 layers of component interconnects (ITRS, 2005).

<sup>20</sup> Memory devices manufactured with the same feature sizes as microprocessors (a logic device) require approximately one-half the number of interconnect layers (ITRS, 2005).

<sup>21</sup> Special attention was given to the manufacturing capacity of plants that use wafers with 300 mm diameters because the actual capacity of these plants in 2004 is below design capacity, the figure provided in WFW. To prevent overstating estimates of partner-capacity shares from plants using 300 mm wafers, *design* capacities contained in WFW were replaced with estimates of *actual installed* capacities for 2004 published by Citigroup Smith Barney (2005). Without this correction, the partner share of capacity would be overstated, by approximately 5 percentage points. For perspective, approximately 95 percent of all new capacity additions in 2004 used 300 mm wafers and by year-end those plants, on average, could operate at but approximately 70 percent of the design capacity.

during this period. Thus, gas specific emissions for 2000 through 2004 were estimated by adding the emissions reported by the Partners to those estimated for the non-Partners.<sup>22</sup>

Partners estimate their emissions using a range of methods. For 2004, most participants cited a method at least as accurate as the IPCC's Tier 2c Methodology, recommended in the IPCC *Good Practice Guidance* (IPCC 2000). The partners with relatively high emissions typically use the more accurate IPCC 2b or 2a methods, multiplying estimates of their PFC consumption by process-specific emission factors that they have either measured or obtained from tool suppliers.

Data used to develop emission estimates were prepared in cooperation with the Partnership. Estimates of operating plant capacities and characteristics for participants and non-participants were derived from the Semiconductor Equipment and Materials Industry (SEMI) *World Fab Watch* (formerly *International Fabs on Disk*) database (1996 to 2004). Estimates of silicon consumed by line-width from 1990 through 2004 were derived from information from VLSI Research (2005), and the number of layers per line-width was obtained from International Technology Roadmap for Semiconductors: 1998-2004 (Burton and Beizaie 2001, ITRS 2005).

## Uncertainty

A quantitative uncertainty analysis of this source category was performed using the IPCC-recommended Tier 2 uncertainty estimation methodology, the Monte Carlo

Stochastic Simulation technique. The equation used to estimate both emissions and their uncertainty is:

$$\text{U.S. emissions} = \text{Non-partnership share of MSI-layer capacity} \times \text{PEVM estimate} + \text{Partnership submittal}$$

The Monte Carlo analysis results presented below relied on estimates of uncertainty attributed to the three variables on the right side of the equation. Estimates of uncertainty for the three variables were in turn developed using the estimated uncertainties associated with the individual inputs to each variable, error propagation analysis, and expert judgment. For the first variable, the aggregate PFC emissions data supplied to the partnership, EPA estimated an uncertainty of approximately  $\pm 10$  percent (representing a 95 percent confidence interval). For the second variable, the share of U.S. layer-weighted silicon capacity accounted for by non-Partners, an uncertainty of  $\pm 10$  percent was assumed based on information from the firm that compiled the database (SMA 2003). For the third variable, the relative error associated with the PEVM estimate in 2004, EPA estimated an uncertainty of  $\pm 20$  percent, using the calculus of error propagation and considering the aggregate average emission factor, world silicon consumption, and the U.S. share of layer-weighted silicon capacity.

Consideration was also given to the nature and magnitude of the potential bias that PEVM might have in its estimates of the number of layers associated with devices manufactured at each technology node. The result of a brief analysis indicated that PEVM overstates the average number of layers across all product categories and all manufacturing

**Table 4-76: Tier 2 Quantitative Uncertainty Estimates for HFC, PFC, and SF<sub>6</sub> Emissions from Semiconductor Manufacture (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate <sup>a</sup> (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>b</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Semiconductor Manufacture	HFC, PFC, and SF <sub>6</sub>	4.7	3.8	6.1	-23%	+23%

<sup>a</sup> Because the uncertainty analysis covered all emissions (including NF<sub>3</sub>), the emission estimate presented here does not match that shown in Table 4-74.

<sup>b</sup> Range of emissions estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

<sup>22</sup> In recent years, the Partnership started reporting gas-specific emissions using GWP values from the Third Assessment Report (TAR), while in previous years the values were taken from the Second Assessment Report (SAR). The emissions reported here are restated using GWPs from the SAR.

technologies for 2004 by 0.12 layers or 2.9 percent. This bias is represented in the uncertainty analysis by deducting the absolute bias value from the PEVM emissions estimate when it is incorporated into the Monte Carlo analysis.

The results of the Tier 2 quantitative uncertainty analysis are summarized in Table 4-76. The emissions estimate for total U.S. PFC emissions from semiconductor manufacturing were estimated to be between 3.8 and 6.1 Tg CO<sub>2</sub> Eq. at a 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This range represents 23 percent below to 23 percent above the 2004 emission estimate of 4.7 Tg CO<sub>2</sub> Eq. This range and the associated percentages apply to the estimate of total emissions rather than those of individual gases. Uncertainties associated with individual gases will be somewhat higher than the aggregate, but were not explicitly modeled.

## Planned Improvements

The method to estimate non-partner related emissions (i.e., PEVM) is not expected to change (with the exception of possible future updates to emission factors and added technology nodes). Future improvements to the national emission estimates will primarily be associated with determining the portion of national emissions to attribute to partner report totals (about 80 percent in recent years). As the nature of the partner reports change through time and industry-wide reduction efforts increase, consideration will be given to what emission reduction efforts—if any—are likely to be occurring at non-partner facilities (currently none are assumed to occur).

## 4.21. Aluminum Production (IPCC Source Category 2C3)

Aluminum is a light-weight, malleable, and corrosion-resistant metal that is used in many manufactured products, including aircraft, automobiles, bicycles, and kitchen utensils. In 2004, the United States was the fourth largest producer of primary aluminum, with eight percent of the world total (USGS 2005). The United States was also a major importer of primary aluminum. The production of primary aluminum—in addition to consuming large quantities of electricity—results in process-related emissions of CO<sub>2</sub> and two perfluorocarbons (PFCs): perfluoromethane (CF<sub>4</sub>) and perfluoroethane (C<sub>2</sub>F<sub>6</sub>).

CO<sub>2</sub> is emitted during the aluminum smelting process when alumina (aluminum oxide, Al<sub>2</sub>O<sub>3</sub>) is reduced to aluminum using the Hall-Heroult reduction process. The reduction of the alumina occurs through electrolysis in a molten bath of natural or synthetic cryolite (Na<sub>3</sub>AlF<sub>6</sub>). The reduction cells contain a carbon lining that serves as the cathode. Carbon is also contained in the anode, which can be a carbon mass of paste, coke briquettes, or prebaked carbon blocks from petroleum coke. During reduction, most of this carbon is oxidized and released to the atmosphere as CO<sub>2</sub>.

Process emissions of CO<sub>2</sub> from aluminum production were estimated to be 4.3 Tg CO<sub>2</sub> Eq. (4,346 Gg) in 2004 (see Table 4-77). The carbon anodes consumed during aluminum production consist of petroleum coke and, to a minor extent, coal tar pitch. The petroleum coke portion of the total CO<sub>2</sub> process emissions from aluminum production is considered to be a non-energy use of petroleum coke, and is accounted for here and not under the CO<sub>2</sub> from Fossil Fuel Combustion source category of the Energy sector. Similarly, the coal tar pitch portion of these CO<sub>2</sub> process emissions is accounted for here rather than in the Iron and Steel source category of the Industrial Processes sector.

In addition to CO<sub>2</sub> emissions, the aluminum production industry is also a source of PFC emissions. During the smelting process, when the alumina ore content of the electrolytic bath falls below critical levels required for electrolysis, rapid voltage increases occur, which are termed “anode effects.” These anode effects cause carbon from the anode and fluorine from the dissociated molten cryolite bath to combine, thereby producing fugitive emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>. In general, the magnitude of emissions for a given level of production depends on the frequency and duration

**Table 4-77: CO<sub>2</sub> Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	7.0	7,045
1998	6.4	6,359
1999	6.5	6,458
2000	6.2	6,244
2001	4.5	4,505
2002	4.6	4,596
2003	4.6	4,609
2004	4.3	4,346

of these anode effects. As the frequency and duration of the anode effects increase, emissions increase.

Since 1990, emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> have declined 85 percent and 81 percent, respectively, to 2.4 Tg CO<sub>2</sub> Eq. of CF<sub>4</sub> (0.4 Gg) and 0.4 Tg CO<sub>2</sub> Eq. of C<sub>2</sub>F<sub>6</sub> (0.05 Gg) in 2004, as shown in Table 4-78 and Table 4-79. This decline is due both to reductions in domestic aluminum production and to actions taken by aluminum smelting companies to reduce the frequency and duration of anode effects. Since 1990, aluminum production has declined by 38 percent, while the average CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emission rates (per metric ton of aluminum produced) have been reduced by 76 and 69 percent respectively.

U.S. primary aluminum production for 2004—totaling 2.5 million metric tons—declined nearly 7 percent from 2003 production. Due to high electric power costs in various regions of the country, aluminum production has been curtailed at several U.S. smelters, which resulted in 2004 production levels that were approximately 31 percent lower

**Table 4-78: PFC Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq.)**

Year	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>	Total
1990	16.2	2.2	18.4
1998	8.1	1.0	9.1
1999	8.0	1.0	9.0
2000	8.1	0.9	9.0
2001	3.5	0.5	4.0
2002	4.6	0.7	5.3
2003	3.3	0.5	3.8
2004	2.4	0.4	2.8

Note: Totals may not sum due to independent rounding.

**Table 4-79: PFC Emissions from Aluminum Production (Gg)**

Year	CF <sub>4</sub>	C <sub>2</sub> F <sub>6</sub>
1990	2.5	0.2
1998	1.2	0.1
1999	1.2	0.1
2000	1.2	0.1
2001	0.5	0.1
2002	0.7	0.1
2003	0.5	0.1
2004	0.4	+

+ Does not exceed 0.5 Gg

than 2000 levels. The transportation industry remained the largest domestic consumer of primary aluminum, accounting for about 38 percent of U.S. consumption (USGS 2005).

## Methodology

CO<sub>2</sub> emissions released during aluminum production were estimated using the combined application of process-specific emissions estimates modeling with individual partner reported data. These estimates are achieved through information gathered by EPA's Voluntary Aluminum Industrial Partnership (VAIP) program.

Most of the CO<sub>2</sub> emissions released during aluminum production occur during the electrolysis reaction of the carbon anode, as described by the following reaction.



For prebake smelter technologies, CO<sub>2</sub> is also emitted during the anode baking process. These emissions can account for approximately 10 percent of total process CO<sub>2</sub> emissions from prebake smelters. The CO<sub>2</sub> emission factor employed was estimated from the production of primary aluminum metal and the carbon consumed by the process. Emissions vary depending on the specific technology used by each plant (e.g., prebake or Söderberg). CO<sub>2</sub> process emissions were estimated using methodology recommended by the *Aluminum Sector Greenhouse Gas Protocol* (IAI, 2003).

The prebake process specific formula recommended by IAI (2003) accounts for various parameters, including net carbon consumption, and the sulfur, ash, and impurity content of the baked anode. For anode baking emissions, process formulas account for packing coke consumption, the sulfur and ash content of the packing coke, as well as the pitch content and weight of baked anodes produced. The Söderberg process formula accounts for the weight of paste consumed per metric ton of aluminum produced, and pitch properties, including sulfur, hydrogen, and ash content.

In 2002, VAIP expanded its voluntary reporting to include direct CO<sub>2</sub> data. As agreed, process data have been reported for 1990, 2000, 2003, and 2004. Where available, smelter specific process data reported under the VAIP were used; however, if the data were incomplete or unavailable, information was supplemented using industry average values recommended by IAI (2003). Smelter specific CO<sub>2</sub> process data were provided by 18 of the 23 operating smelters in 1990



and 2000, and 15 out of 16 operating smelters in 2003 and 2004. For years where CO<sub>2</sub> process data were not reported by these companies, estimates were developed through linear interpolation, and/or assuming industry default values.

In the absence of any smelter specific process data (i.e., 1 out of 16 smelters in 2004, and 5 out of 23 between 1990 and 2003), CO<sub>2</sub> emission estimates were estimated using the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997), which provide CO<sub>2</sub> emission factors for each technology type. During alumina reduction in a prebake anode cell process, approximately 1.5 metric tons of CO<sub>2</sub> are emitted for each metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997). Similarly, during alumina reduction in a Soderberg cell process, approximately 1.8 metric tons of CO<sub>2</sub> are emitted per metric ton of aluminum produced (IPCC/UNEP/OECD/IEA 1997).

Aluminum production data for 15 out of the 16 operating smelters were reported under the VAIP in 2004. For the non-reporting smelter, production was estimated based on the difference between reporting smelters and national aluminum production levels. Between 1990 and 2003, production data were provided by 21 of the 23 operating U.S. smelters.

PFC emissions from aluminum production were estimated using a per-unit production emission factor that is expressed as a function of operating parameters (anode effect frequency and duration), as follows:

$$\text{PFC (CF}_4 \text{ or C}_2\text{F}_6\text{) kg/metric ton Al} = S \times \text{Anode Effect Minutes/Cell-Day}$$

where,

$$S = \text{Slope coefficient (kg PFC/metric ton Al/(Anode Effect minutes/cell day))}$$

$$\begin{aligned} &\text{Anode Effect Minutes/Cell-Day} = \\ &\text{Anode Effect Frequency/Cell-Day} \times \\ &\text{Anode Effect Duration (minutes)} \end{aligned}$$

Smelter-specific slope coefficients that are based on field measurements yield the most accurate results. To estimate emissions between 1990 and 2003, smelter-specific coefficients were available and were used for 12 out of the 23 U.S. smelters. To estimate 2004 emissions, smelter-specific coefficients were available and were used for 5 out of the 16 operating U.S. smelters, representing approximately 35 percent of 2004 U.S. production. For the remaining 11 operating smelters, technology-specific

slope coefficients from the *IPCC Good Practice Guidance* (IPCC 2000) were applied. The slope coefficients were combined with smelter-specific anode effect data collected by aluminum companies and reported under the VAIP, to estimate emission factors over time. In 2004, smelter-specific anode effect data was available for 15 of the 16 operating smelters. Where smelter-specific anode effect data were not available (i.e., 1 out of 16 smelters in 2004, 2 out of 23 smelters between 1990 and 2003), industry averages were used. For all smelters, emission factors were multiplied by annual production to estimate annual emissions at the smelter level. In 2004, smelter-specific production data was available for 15 of the 16 operating smelters; production at the one remaining smelter was estimated based on national aluminum production and capacity data (USAA 2005). Between 1990 and 2004, production data has been provided by 21 of the 23 U.S. smelters. Emissions were then aggregated across smelters to estimate national emissions. The methodology used to estimate emissions is consistent with the methodologies recommended by the *IPCC Good Practice Guidance* (IPCC 2000).

National primary aluminum production data for 1990 through 2001 (see Table 4-80) obtained from USGS, *Mineral Industry Surveys: Aluminum Annual Report* (USGS 1995, 1998, 2000, 2001, 2002). For 2002, 2003, and 2004, national aluminum production data were obtained from the United States Aluminum Association's *Primary Aluminum Statistics* (USAA 2004, 2005). The CO<sub>2</sub> emission factors were taken

**Table 4-80: Production of Primary Aluminum (Gg)**

Year	Gg
1990	4,048
1991	4,121
1992	4,042
1993	3,695
1994	3,299
1995	3,375
1996	3,577
1997	3,603
1998	3,713
1999	3,779
2000	3,668
2001	2,637
2002	2,705
2003	2,705
2004	2,517

from the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OECD/IEA 1997).

## Uncertainty

The overall uncertainties associated with the 2004 CO<sub>2</sub>, CF<sub>4</sub>, and C<sub>2</sub>F<sub>6</sub> emission estimates were calculated using the IPCC Good Practice Guidance Tier 2 methodology. Uncertainty associated with the parameters used to estimate CO<sub>2</sub> emissions included that associated with production data, with the share of U.S. aluminum production attributable to each smelter type, and with the emission factors applied to production data to calculate emissions. Uncertainty surrounding production data was assumed to be characterized as described below, while other variables were modeled assuming triangular distributions. Emission factors were determined through expert elicitation to be 50 percent certain at a 95 percent confidence level, while the share of production attributed to smelter types were determined to be associated with a 25 percent uncertainty. A Monte Carlo analysis was applied to estimate the overall uncertainty of the CO<sub>2</sub> emissions estimate for the U.S. aluminum industry as a whole and the results are provided below.

To estimate the uncertainty associated with emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, EPA estimated the uncertainties associated with three variables for each smelter: (1) the quantity of aluminum produced, (2) the anode effect minutes per cell day (which may be reported directly or calculated as the product of anode effect frequency and anode effect duration), and (3) the smelter- or technology-specific slope coefficient. A Monte Carlo analysis was then applied to estimate the overall uncertainty of the emissions estimate for each smelter and for the U.S. aluminum industry as a whole.

All three types of data are assumed to be characterized by a normal distribution. The uncertainty of aluminum production estimates was assumed to be 1 percent or 25 percent, depending on whether a smelter's production was reported or estimated (Kantamaneni et al., 2001). The uncertainty of the anode effect frequency was assumed to be 2 percent for data that was reported; however, for the one smelter that did not report data, the uncertainty was estimated to be 78 percent (Kantamaneni et al., 2001). Similarly, the uncertainty in anode effect duration was assumed to be 5 percent for data that was reported, but 70 percent for data that was estimated (Kantamaneni et al., 2001). The uncertainties for estimated anode effect

frequency and duration are based on the standard deviations of reported technology-specific anode-effect frequency and duration in the International Aluminum Institute's anode effect survey (IAI 2000).

For the three smelters that participated in the 2003 EPA-funded measurement study, CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> slope coefficient uncertainties were calculated to be 10 percent. For the remaining smelters, given the limited uncertainty data on site-specific slope coefficients (i.e., those developed using IPCC Tier 3b methodology), the overall uncertainty associated with the slope coefficients is conservatively assumed to be similar to that given by the IPCC guidance for technology-specific slope coefficients. Consequently, the uncertainty assigned to the slope coefficients ranged between 10 percent and 35 percent, depending upon the gas and the smelter technology type. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-81. Aluminum production-related CO<sub>2</sub> emissions were estimated to be between 3.0 and 5.6 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 30 percent below to 30 percent above the emission estimate of 4.3 Tg CO<sub>2</sub> Eq. Also, production-related CF<sub>4</sub> emissions were estimated to be between 2.2 and 2.7 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 10 percent below to 12 percent above the emission estimate of 2.4 Tg CO<sub>2</sub> Eq. Finally, aluminum production-related C<sub>2</sub>F<sub>6</sub> emissions were estimated to be between 0.4 and 0.5 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level. This indicates a range of approximately 16 percent below to 18 percent above the emission estimate of 0.43 Tg CO<sub>2</sub> Eq.

This inventory may slightly underestimate greenhouse gas emissions from aluminum production and casting because it does not account for the possible use of SF<sub>6</sub> as a cover gas or a fluxing and degassing agent in experimental and specialized casting operations. The extent of such use in the U.S. is not known. Historically, SF<sub>6</sub> emissions from aluminum activities have been omitted from estimates of global SF<sub>6</sub> emissions, with the explanation that any emissions would be insignificant (Ko et al. 1993, Victor and MacDonald 1998). The concentration of SF<sub>6</sub> in the mixtures is small and a portion of the SF<sub>6</sub> is decomposed in the process (MacNeal

**Table 4-81: Tier 2 Quantitative Uncertainty Estimates for CO<sub>2</sub> and PFC Emissions from Aluminum Production (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Aluminum Production	CO <sub>2</sub>	4.3	3.0	5.6	-30%	+30%
Aluminum Production	CF <sub>4</sub>	2.4	2.2	2.7	-10%	+12%
Aluminum Production	C <sub>2</sub> F <sub>6</sub>	0.4	0.4	0.5	-16%	+18%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.

et al. 1990, Garipey and Dube 1992, Ko et al. 1993, Ten Eyck and Lukens 1996, Zurecki 1996).

## Recalculations Discussion

Relative to the previous Inventory report, CO<sub>2</sub> emission estimates for the period 1990 through 2003 were updated based on revisions to the estimation methodology. Previous CO<sub>2</sub> emission estimates were based on methodology and default emission factors defined by the *Revised 1996 IPCC Guidelines* (IPCC/UNEP/OED/IEA 1997). Current estimates were developed using a combination of process specific formulas (IAI 2003) and default emission factors (IPCC/UNEP/OED/IEA 1997). The former approach was used where smelter-specific process data was available. Based on this revision, CO<sub>2</sub> emissions from aluminum production have increased by approximately 10 percent for each year during the 1990 to 2003 period relative to the previous report.

The smelter-specific emission factors used for estimating PFC emissions, as well as aluminum production levels, were revised to reflect recently-reported data concerning smelter operating parameters. The combination of these changes resulted in an average annual increase of approximately of less than 0.05 Tg CO<sub>2</sub> Eq. (0.4 percent) in PFC emissions from aluminum production for the period 1990 through 2003 relative to the previous report.

## 4.22. Magnesium Production and Processing (IPCC Source Category 2C4)

The magnesium metal production and casting industry uses sulfur hexafluoride (SF<sub>6</sub>) as a cover gas to prevent the rapid oxidation of molten magnesium in the presence of air. A dilute gaseous mixture of SF<sub>6</sub> with dry air and/or CO<sub>2</sub> is

blown over molten magnesium metal to induce and stabilize the formation of a protective crust. A small portion of the SF<sub>6</sub> reacts with the magnesium to form a thin molecular film of mostly magnesium oxide and magnesium fluoride. The amount of SF<sub>6</sub> reacting in magnesium production and processing is assumed to be negligible and thus all SF<sub>6</sub> used is assumed to be emitted into the atmosphere. Sulfur hexafluoride has been used in this application around the world for the last twenty years. It has largely replaced salt fluxes and SO<sub>2</sub>, which are more toxic and corrosive than SF<sub>6</sub>.

The magnesium industry emitted 2.7 Tg CO<sub>2</sub> Eq. (0.1 Gg) of SF<sub>6</sub> in 2004, representing a decrease of approximately 10 percent from 2003 emissions (see Table 4-82). The reduction in emissions compared to 2003 occurred despite a 3 percent increase in the amount of metal processed in 2004. There are currently plans to expand primary magnesium production in the United States to meet demand for magnesium metal by U.S. casting companies, which are in turn meeting demand for magnesium parts by the automotive sector. Recent antidumping duties imposed on Chinese imports by the U.S. International Trade Commission

**Table 4-82: SF<sub>6</sub> Emissions from Magnesium Production and Processing (Tg CO<sub>2</sub> Eq. and Gg)**

Year	Tg CO <sub>2</sub> Eq.	Gg
1990	5.4	0.2
1998	5.8	0.2
1999	6.0	0.3
2000	3.2	0.1
2001	2.6	0.1
2002	2.6	0.1
2003	3.0	0.1
2004	2.7	0.1

have shifted some U.S. demand to Canadian imports (USGS 2005). Anticipated increases in domestic primary production capacity combined with Canadian imports should be able to meet near-term U.S. demand (USGS 2005).

## Methodology

Emission estimates for the magnesium industry incorporate information provided by industry participants in EPA's SF<sub>6</sub> Emission Reduction Partnership for the Magnesium Industry. The Partnership started in 1999 and, currently, participating companies represent 100 percent of U.S. primary production and 90 percent of the casting sector (i.e., die, sand, permanent mold, wrought, and anode casting). Emissions for 1999 through 2004 from primary production, some secondary production (i.e., recycling), and die casting were reported by Partnership participants. Emission factors for 2002 to 2004 for sand casting activities were also acquired through the Partnership. The 1999 through 2004 emissions from the remaining secondary production and casting were estimated by multiplying industry emission factors (kg SF<sub>6</sub> per metric ton of Mg produced or processed) by the amount of metal produced or consumed in the six major processes (other than primary production) that require SF<sub>6</sub> melt protection: (1) secondary production, (2) die casting, (3) sand casting, (4) permanent mold, (5) wrought products, and (6) anodes. The emission factors are provided below in Table 4-83. The emission factors for primary production and sand casting are withheld to protect company-specific production information. However, the emission factor for primary production has not risen above the 1995 value of 1.1 kg SF<sub>6</sub> per metric ton.

Die casting emissions for 1999 through 2004, which accounted for 48 to 75 percent of all SF<sub>6</sub> emissions from U.S. casting and recycling processes during this period,

were estimated based on information supplied by industry Partners. From 2000 to 2004, Partners accounted for all U.S. die casting that was tracked by USGS. In 1999, Partners did not account for all die casting tracked by USGS, and, therefore, it was necessary to estimate the emissions of die casters who were not Partners. Die casters who were not Partners were assumed to be similar to partners who cast small parts. Due to process requirements, these casters consume larger quantities of SF<sub>6</sub> per metric ton of processed magnesium than casters that process large parts. Consequently, emissions estimates from this group of die casters were developed using an average emission factor of 5.2 kg SF<sub>6</sub> per metric ton of magnesium. The emission factors for the other industry sectors (i.e., secondary production, permanent mold, wrought, and anode casting) were based on discussions with industry representatives.

Data used to develop these emission estimates were provided by the Magnesium Partnership participants and the USGS. U.S. magnesium metal production (primary and secondary) and consumption (casting) data from 1990 through 2004 were available from the USGS (USGS 2002, 2003, 2005a, 2005b). Emission factors from 1990 through 1998 were based on a number of sources. Emission factors for primary production were available from U.S. primary producers for 1994 and 1995, and an emission factor for die casting of 4.1 kg per metric ton was available for the mid-1990s from an international survey (Gjestland & Magers 1996).

To estimate emissions for 1990 through 1998, industry emission factors were multiplied by the corresponding metal production and consumption (casting) statistics from USGS. The primary production emission factors were 1.2 kg per metric ton for 1990 through 1993, and 1.1 kg per metric ton for 1994 through 1996. For die casting, an emission

**Table 4-83: SF<sub>6</sub> Emission Factors (kg SF<sub>6</sub> per metric ton of magnesium)**

Year	Secondary	Die Casting	Permanent Mold	Wrought	Anodes
1999	1	2.14 <sup>a</sup>	2	1	1
2000	1	0.73	2	1	1
2001	1	0.77	2	1	1
2002	1	0.70	2	1	1
2003	1	0.84	2	1	1
2004	1	0.78	2	1	1

<sup>a</sup> Weighted average that includes an estimated emission factor of 5.2 kg SF<sub>6</sub> per metric ton of magnesium for die casters that do not participate in the Partnership.

factor of 4.1 kg per metric ton was used for the period 1990 through 1996. For 1996 through 1998, the emission factors for primary production and die casting were assumed to decline linearly to the level estimated based on partner reports in 1999. This assumption is consistent with the trend in SF<sub>6</sub> sales to the magnesium sector that is reported in the RAND survey of major SF<sub>6</sub> manufacturers, which shows a decline of 70 percent from 1996 to 1999 (RAND 2004). Sand casting emission factors for 2002 through 2004 were provided by the magnesium partnership participants and 1990 through 2001 emission factors for this process were assumed to have been the same as the 2002 emission factor. The emission factors for the other processes (i.e., secondary production, and permanent mold, wrought, and anode casting), about which less is known, were assumed to remain constant at levels defined in Table 4-83.

## Uncertainty

To estimate the uncertainty of the estimated 2004 SF<sub>6</sub> emissions from magnesium production and processing, EPA estimated the uncertainties associated with three variables (1) emissions reported by magnesium producers and processors that participate in the SF<sub>6</sub> Emission Reduction Partnership, (2) emissions estimated for magnesium producers and processors that participate in the Partnership but did not report this year, and (3) emissions estimated for magnesium producers and processors that do not participate in the Partnership. An uncertainty of 5 percent was assigned to the data reported by each participant in the SF<sub>6</sub> Emission Reduction Partnership. If partners did not report emissions data during the current reporting year, SF<sub>6</sub> emissions data were estimated using available emission factor and production information reported in prior years. The uncertainty associated with the extrapolated emission factor was assumed to be 25 percent, while that associated with the extrapolated production was assumed to be 30

percent. Between 1999 and 2004, non-reporting partners have accounted for between 0 and 17 percent of total estimated sector emissions. For those industry processes that are not represented in EPA's partnership, such as permanent mold, anode, and wrought casting, SF<sub>6</sub> emissions were estimated using production and consumption statistics reported by USGS and estimated process-specific emission factors (see Table 4-83). The uncertainties associated with the emission factors and USGS-reported statistics were assumed to be 75 percent and 25 percent, respectively. In general, where precise quantitative information was not available on the uncertainty of a parameter, a conservative (upper-bound) value was used.

Additional uncertainties exist in these estimates, such as the basic assumption that SF<sub>6</sub> neither reacts nor decomposes during use. The melt surface reactions and high temperatures associated with molten magnesium could potentially cause some gas degradation. Recent measurement studies have identified SF<sub>6</sub> cover gas degradation at hot-chambered die casting machines on the order of 10 percent (Bartos et al. 2003). As is the case for other sources of SF<sub>6</sub> emissions, total SF<sub>6</sub> consumption data for magnesium production and processing in the United States were not available. Sulfur hexafluoride may also be used as a cover gas for the casting of molten aluminum with high magnesium content; however, to what extent this technique is used in the United States is unknown.

The results of this Tier 2 quantitative uncertainty analysis are summarized in Table 4-84. SF<sub>6</sub> emissions associated with magnesium production and processing were estimated to be between 2.4 and 3.1 Tg CO<sub>2</sub> Eq. at the 95 percent confidence level (or in 19 out of 20 Monte Carlo Stochastic Simulations). This indicates a range of approximately 11 percent below to 13 percent above the 2004 emissions estimate of 2.7 Tg CO<sub>2</sub> Eq.

**Table 4-84: Tier 2 Quantitative Uncertainty Estimates for SF<sub>6</sub> Emissions from Magnesium Production and Processing (Tg CO<sub>2</sub> Eq. and Percent)**

Source	Gas	2004 Emission Estimate (Tg CO <sub>2</sub> Eq.)	Uncertainty Range Relative to Emission Estimate <sup>a</sup>			
			(Tg CO <sub>2</sub> Eq.)		(%)	
			Lower Bound	Upper Bound	Lower Bound	Upper Bound
Magnesium Production	SF <sub>6</sub>	2.7	2.4	3.1	-11%	+13%

<sup>a</sup> Range of emission estimates predicted by Monte Carlo Stochastic Simulation for a 95 percent confidence interval.



## Box 4-1: Potential Emission Estimates of HFCs, PFCs, and SF<sub>6</sub>

Emissions of HFCs, PFCs and SF<sub>6</sub> from industrial processes can be estimated in two ways, either as potential emissions or as actual emissions. Emission estimates in this chapter are “actual emissions,” which are defined by the *Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories* (IPCC/UNEP/OECD/IEA 1997) as estimates that take into account the time lag between consumption and emissions. In contrast, “potential emissions” are defined to be equal to the amount of a chemical consumed in a country, minus the amount of a chemical recovered for destruction or export in the year of consideration. Potential emissions will generally be greater for a given year than actual emissions, since some amount of chemical consumed will be stored in products or equipment and will not be emitted to the atmosphere until a later date, if ever. Although actual emissions are considered to be the more accurate estimation approach for a single year, estimates of potential emissions are provided for informational purposes.

Separate estimates of potential emissions were not made for industrial processes that fall into the following categories:

- *By-product emissions.* Some emissions do not result from the consumption or use of a chemical, but are the unintended by-products of another process. For such emissions, which include emissions of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> from aluminum production and of HFC-23 from HCFC-22 production, the distinction between potential and actual emissions is not relevant.
- *Potential emissions that equal actual emissions.* For some sources, such as magnesium production and processing, no delay between consumption and emission is assumed and, consequently, no destruction of the chemical takes place. In this case, actual emissions equal potential emissions.

Table 4-85 presents potential emission estimates for HFCs and PFCs from the substitution of ozone depleting substances, HFCs, PFCs, and SF<sub>6</sub> from semiconductor manufacture, and SF<sub>6</sub> from magnesium production and processing and electrical transmission and distribution.<sup>23</sup> Potential emissions associated with the substitution for ozone depleting substances were calculated using the EPA's Vintaging Model. Estimates of HFCs, PFCs, and SF<sub>6</sub> consumed by semiconductor manufacture were developed by dividing chemical-by-chemical emissions by the appropriate chemical-specific emission factors from the IPCC *Good Practice Guidance* (Tier 2c). Estimates of CF<sub>4</sub> consumption were adjusted to account for the conversion of other chemicals into CF<sub>4</sub> during the semiconductor manufacturing process, again using the default factors from the IPCC *Good Practice Guidance*. Potential SF<sub>6</sub> emissions estimates for electrical transmission and distribution were developed using U.S. utility purchases of SF<sub>6</sub> for electrical equipment. From 1999 through 2004, estimates were obtained from reports submitted by participants in EPA's SF<sub>6</sub> Emission Reduction Program for Electric Power Systems. U.S. utility purchases of SF<sub>6</sub> for electrical equipment from 1990 through 1998 were backcasted based on world sales of SF<sub>6</sub> to utilities. Purchases of SF<sub>6</sub> by utilities were added to SF<sub>6</sub> purchases by electrical equipment manufacturers to obtain total SF<sub>6</sub> purchases by the electrical equipment sector.

**Table 4-85: 2004 Potential and Actual Emissions of HFCs, PFCs, and SF<sub>6</sub> from Selected Sources (Tg CO<sub>2</sub> Eq.)**

Source	Potential	Actual
Substitution of Ozone Depleting Substances	192.0	103.3
Aluminum Production	–	2.8
HCFC-22 Production	–	15.6
Semiconductor Manufacture	7.3	4.7
Magnesium Production and Processing	2.7	2.7
Electrical Transmission and Distribution	23.3	13.8

– Not applicable.

## Recalculations Discussion

The emission calculation methodology was revised to reflect more accurate emission factor data for sand casting activities. Sand casting activity data now utilizes partner reported emission factors from 1990 through 2003 resulting

in a slight increase in historical emissions of about 1 percent or less depending on the year. The emission estimate for 2002 was also adjusted downward slightly from the previously reported values. This revision reflects an update to historical secondary production data supplied by USGS. The change

<sup>23</sup> See Annex 5 for a discussion of sources of SF<sub>6</sub> emissions excluded from the actual emissions estimates in this report.

resulted in a decrease of 0.1 Tg CO<sub>2</sub> Eq. (5 percent) in SF<sub>6</sub> emissions from magnesium production and processing for 2002 relative to the previous report.

## Planned Improvements

As more work assessing the degree of cover gas degradation and associated byproducts is undertaken and published, results could potentially be used to refine the emission estimates, which currently assume (per IPCC *Good Practice Guidance*, IPCC 2000) that all SF<sub>6</sub> utilized is emitted to the atmosphere. EPA-funded measurements of SF<sub>6</sub> in hot chamber die casting have indicated that the latter assumption may be incorrect, with observed SF<sub>6</sub> degradation on the order of 10 percent (Bartos et al. 2003). More recent EPA-funded measurement studies have confirmed this observation for cold chamber die casting (EPA 2004). Another issue that will be addressed in future inventories is the likely adoption of alternate cover gases by U.S. magnesium producers and processors. These cover gases, which include Am-Cover™ (containing HFC-134a) and Novec™ 612, have lower GWPs than SF<sub>6</sub>, and tend to quickly decompose during their exposure to the molten metal. Additionally, as more companies join the partnership, in

particular those from sectors not currently represented, such as permanent mold and anode casting, emission factors will be refined to incorporate these additional data.

## 4.23. Industrial Sources of Indirect Greenhouse Gases

In addition to the main greenhouse gases addressed above, many industrial processes generate emissions of indirect greenhouse gases. Total emissions of nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), and non-CH<sub>4</sub> volatile organic compounds (NMVOCs) from non-energy industrial processes from 1990 to 2004 are reported in Table 4-86.

### Methodology

These emission estimates were obtained from preliminary data (EPA 2005), and disaggregated based on EPA (2003), which, in its final iteration, will be published on the National Emission Inventory (NEI) Air Pollutant Emission Trends web site. Emissions were calculated either for individual categories or for many categories combined, using basic activity data (e.g., the amount of raw material processed) as an indicator of emissions. National activity data were

**Table 4-86: NO<sub>x</sub>, CO, and NMVOC Emissions from Industrial Processes (Gg)**

Gas/Source	1990	1998	1999	2000	2001	2002	2003	2004
<b>NO<sub>x</sub></b>	<b>591</b>	<b>637</b>	<b>595</b>	<b>626</b>	<b>656</b>	<b>630</b>	<b>631</b>	<b>632</b>
Chemical & Allied Product Manufacturing	152	117	93	95	97	95	96	96
Metals Processing	88	81	78	81	86	76	76	76
Storage and Transport	3	15	13	14	15	14	14	14
Other Industrial Processes	343	424	409	434	457	442	442	443
Miscellaneous*	5	1	2	2	1	3	3	3
<b>CO</b>	<b>4,124</b>	<b>3,163</b>	<b>2,156</b>	<b>2,217</b>	<b>2,339</b>	<b>2,286</b>	<b>2,286</b>	<b>2,286</b>
Chemical & Allied Product Manufacturing	1,074	981	317	327	338	306	306	306
Metals Processing	2,395	1,544	1,138	1,175	1,252	1,174	1,174	1,174
Storage and Transport	69	65	148	154	162	195	195	195
Other Industrial Processes	487	535	518	538	558	576	576	576
Miscellaneous*	101	38	35	23	30	35	35	35
<b>NMVOCs</b>	<b>2,426</b>	<b>2,047</b>	<b>1,813</b>	<b>1,773</b>	<b>1,769</b>	<b>1,723</b>	<b>1,725</b>	<b>1,727</b>
Chemical & Allied Product Manufacturing	575	357	228	230	238	194	195	195
Metals Processing	111	71	60	61	65	62	63	63
Storage and Transport	1,356	1,204	1,122	1,067	1,082	1,093	1,094	1,096
Other Industrial Processes	364	402	398	412	381	369	369	370
Miscellaneous*	20	13	6	3	4	5	5	5

\* Miscellaneous includes the following categories: catastrophic/accidental release, other combustion, health services, cooling towers, and fugitive dust. It does not include agricultural fires or slash/prescribed burning, which are accounted for under the Field Burning of Agricultural Residues source.

Note: Totals may not sum due to independent rounding.

collected for individual categories from various agencies. Depending on the category, these basic activity data may include data on production, fuel deliveries, raw material processed, etc.

Activity data were used in conjunction with emission factors, which together relate the quantity of emissions to the activity. Emission factors are generally available from the EPA's *Compilation of Air Pollutant Emission Factors, AP-42* (EPA 1997). The EPA currently derives the overall emission control efficiency of a source category from a variety of

information sources, including published reports, the 1985 National Acid Precipitation and Assessment Program emissions inventory, and other EPA databases.

## Uncertainty

Uncertainties in these estimates are partly due to the accuracy of the emission factors used and accurate estimates of activity data. A quantitative uncertainty analysis was not performed.

This page intentionally left blank.